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CARBON FIBERS WITH CONTROLLED SURFACE CHEMISTRY

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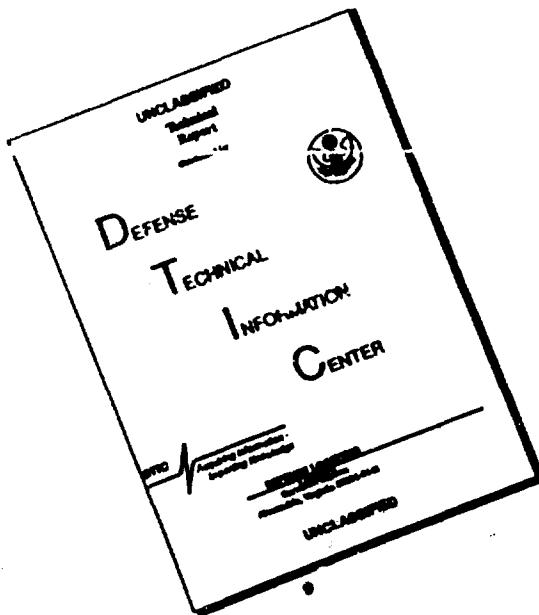
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Program Objective

Relatively little is known about the structure and properties of composite interphase regions or their affects on overall composite properties. The program objectives are to generate sets of carbon fibers with a range of controlled surface chemistries using glow discharge plasmas. Such treatments have been shown to produce a variety of surface functionalities that cannot be achieved with other methods. Acidic and basic surfaces will be created and characterized for chemistry, energy, and morphology compared to conventionally used treatments. Well characterized sets of fibers will be delivered to the Naval Air Warfare Center.

Task 1 - Treatment Section

The literature search on carbon fiber plasma treatments referenced 56 articles in Chemical Abstracts. Analysis of the citations reveals that no unusual plasma compositions are documented in the literature. The reported plasmas are primarily oxidizing types or ammonia. Ammonia, oxygen, and CO₂ plasmas were therefore selected for surface chemistry treatments based on the literature search and conversations between NAWC personnel and Dr. Ron Allred.

Task 2 - Fiber Surface Treatments/Treatment Optimization

Carbon fiber, AS4-12K, was subjected to the RF-plasma discharge treatments identified in Task 1 by treating them in the continuous plasma reactor, shown in Figure 1. The continuous plasma reactor consists of three separate chambers, each 1 meter long, which may contain plasmas of different composition. Different plasmas are employed in two instances: 1) to clean the fiber surface prior to functionalization, or 2) to impart sequential treatments to the fiber, i.e., unique polymerized coatings may be bonded to the fiber. Process parameters from the literature search were used as guidelines for optimizing the plasma treatments selected in Task 1. The experimental matrix consisted of the following three parameters: RF-power, gas flow rate, and gas pressure. RF-power, gas flow rate, and gas pressure were generally varied between 50-200 watts, 5 and 200 sccm, 85-10000 mtorr, respectively.

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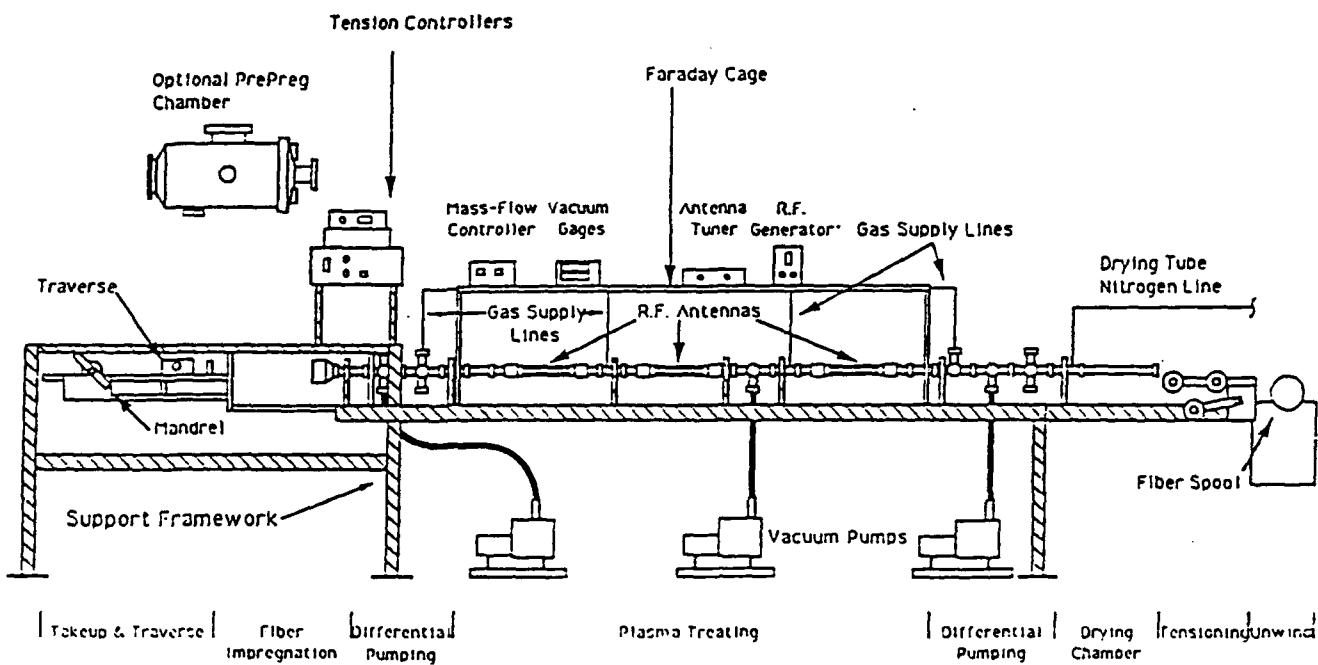


Figure 1. Continuous Plasma Treatment Facility

Ammonia Plasma

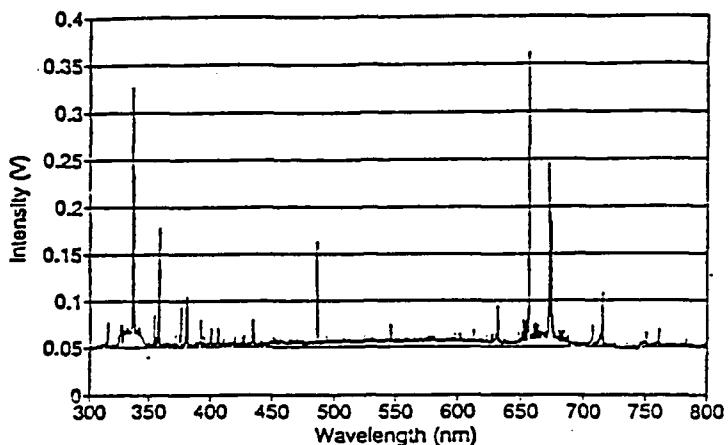
The ammonia plasma was characterized in each tube using UV-visible emission spectroscopy. Spectra for each tube with no carbon fiber present are shown in Figure 2. Ammonia decomposition reactions are characterized by the appearance of hydrogen (spectral lines at 656.3 nm and 486.1 nm) and nitrogen (spectral lines appear between 440 nm and 325 nm with the most prominent peak at 337 nm). Primary amine radicals are associated with the appearance of hydrogen while the appearance of nitrogen indicates the complete decomposition of ammonia. From Figure 2 the relative nitrogen to hydrogen peak ration decreases along the reactor length indicating extensive ammonia decomposition. To prevent ammonia decomposition to nitrogen, ammonia pressure was kept high and ammonia flow in the reactor was counter to the fiber draw direction.

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First Tube

100W, 30 SCCM, 170 mT

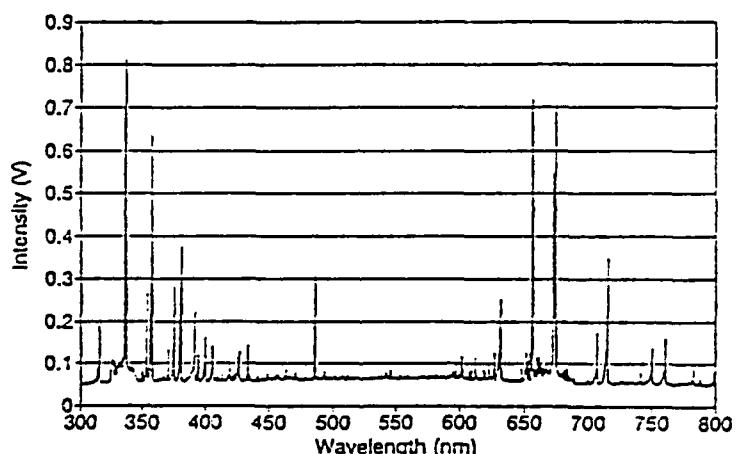
(a)



Second Tube

100W, 30 SCCM, 170 mT

(b)



Third Tube

100W, 30 SCCM, 170 mT

(c)

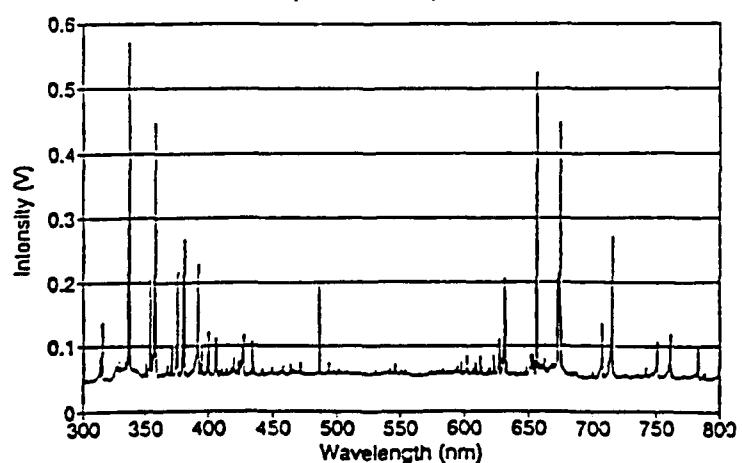


Figure 2. Ammonia emission spectra along the reactor length:
(a) tube 1, (b) tube 2, (c) tube 3.

Subsequent to an argon cleaning in tube 1, the fiber was subjected to the ammonia experimental matrix given in Table I for 60 second treatments. The observed emission spectra were of little quantitative value, as shown in Figures 3 and 4 for treatments 1 and 4, respectively. Neither spectrum shows the distinctive amine step at 575 nm as illustrated in Figure 5 for a standard ammonia plasma. Light emitted from the burning loose fibers obscures the plasma emission and prevents the use of emission spectroscopy as a process control technique.

TABLE I
AMINATION OF AS4 CARBON FIBERS

<u>Plasma Parameters</u>	<u>Avg. Absorption/Fiber Weight</u>
1) 5 sccm, 85 mtorr, 200 W	0.078
2) 50 sccm, 300 mtorr, 60 W	0.058
3) 50 sccm, 300 mtorr, 60 W	0.067
4) 25 sccm, 1000 mtorr, 200 W	0.224
5) 50 sccm, 1000 mtorr, 200 W	0.192
6) 50 sccm, 1000 mtorr, 100 W	0.224
7) 200 sccm, 1000 mtorr, 230 W	0.221

The surface amine concentration was measured using an azo dye (Ponceau 3R) following the procedure in "Polymer Preprints," 24, 1, March 1983. Surface amine concentration as a function of process parameters, given in terms of average of absorption/fiber weight for 5 samples at each plasma condition, are given in Table I. The larger the absorption, the higher the amine concentration. Results show that high ammonia pressure is needed to achieve high concentrations of amine sites, and that amination is independent of power and flow rate. Plasma power levels between 100-230 W are sufficient to disassociate ammonia gas to primary amine radicals. High gas pressure results in significant recombination reaction rates, irrespective of gas flow rate, to prevent amine radical decombination to nitrogen.

The ammonia treated AS4-12K carbon fibers delivered to NAWC were subjected to the following plasma: 5 sccm, >1000 mtorr, 200 W. The emission spectra for this plasma, without fiber present, is given in Figure 6. The average absorption/fiber weight was measured to be 0.316 which corresponds to a surface amine concentration of 0.169 sites/nm².

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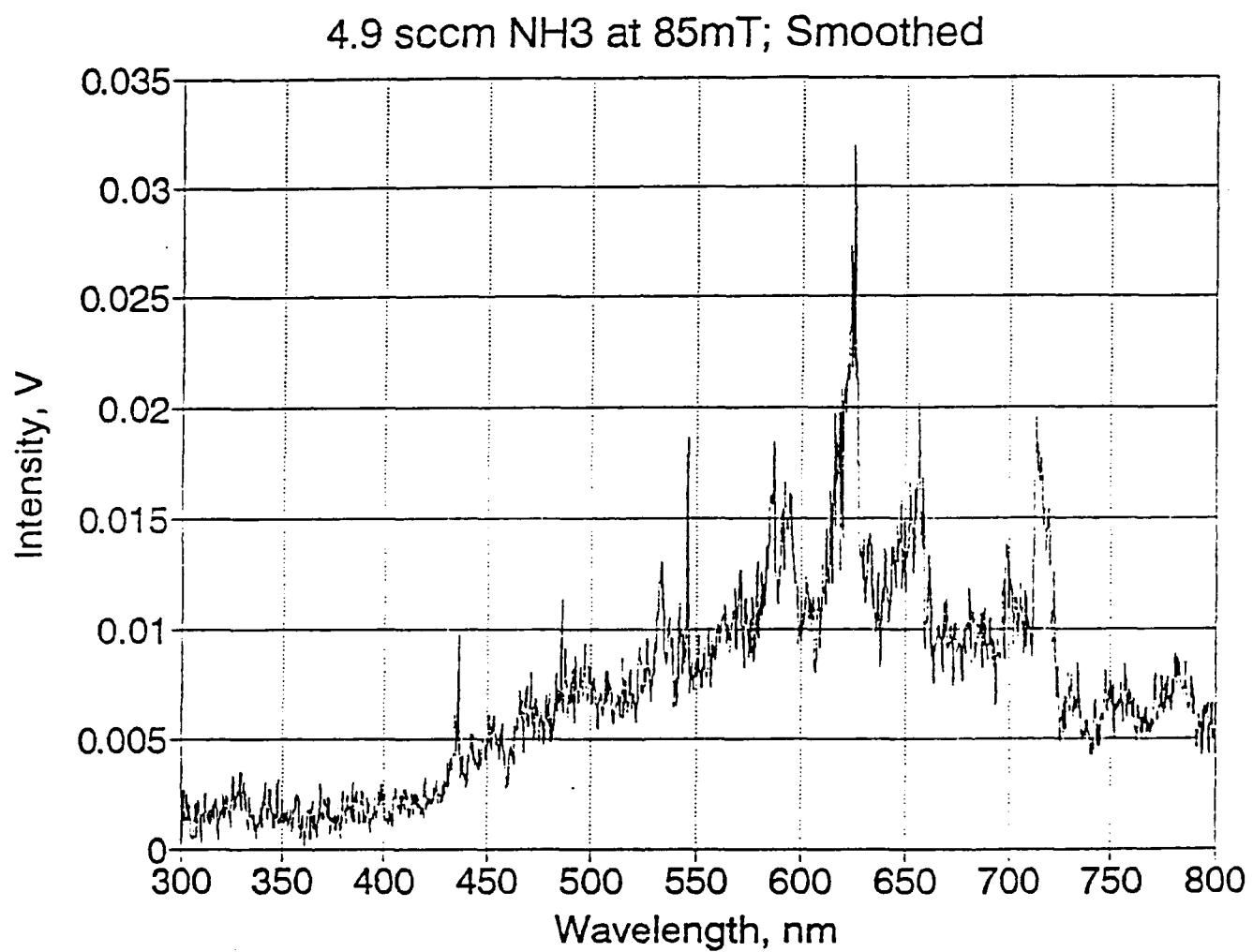


Figure 3. Low pressure ammonia plasma emission spectrum.

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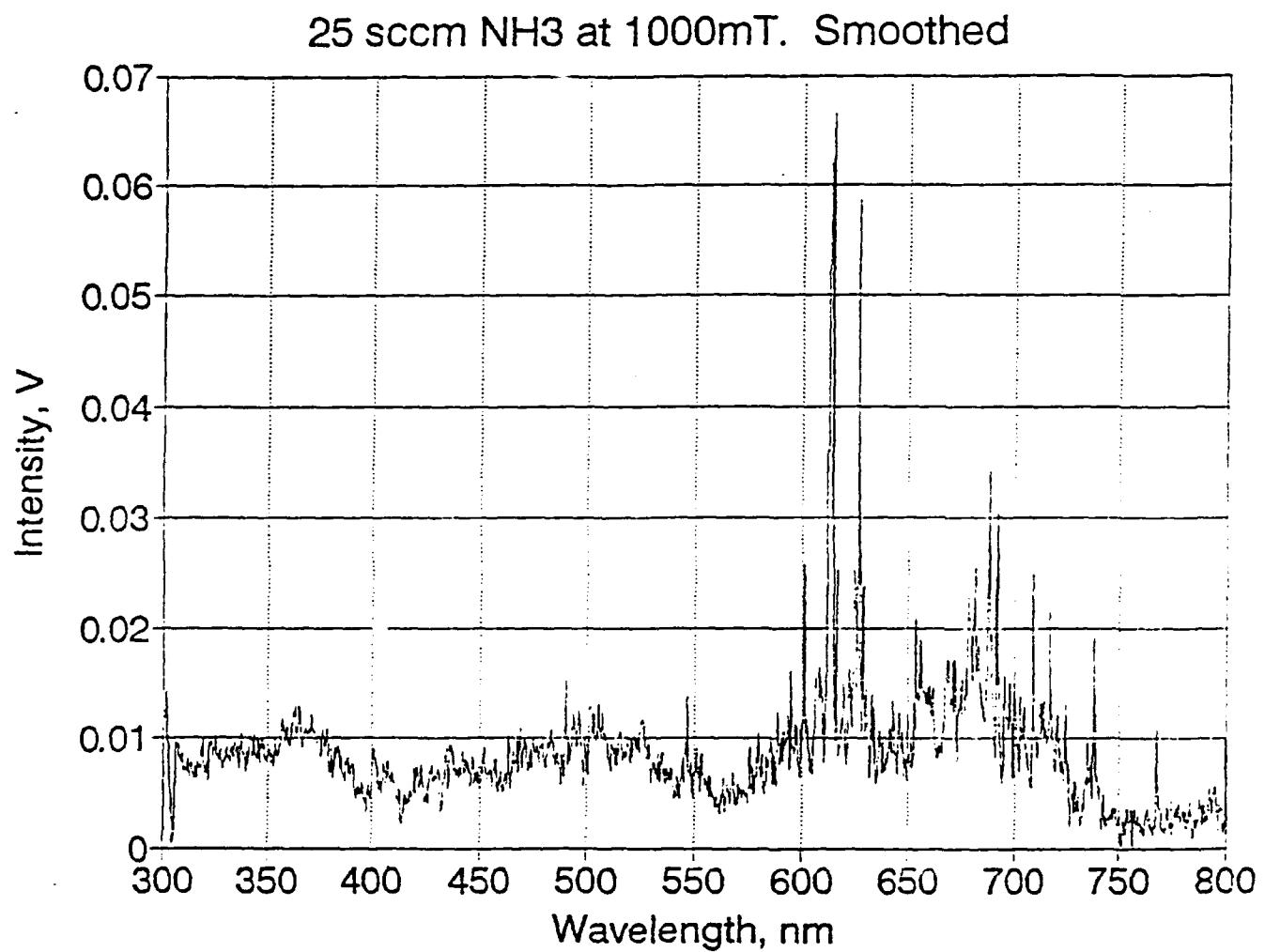


Figure 4. High pressure ammonia plasma emission spectrum.

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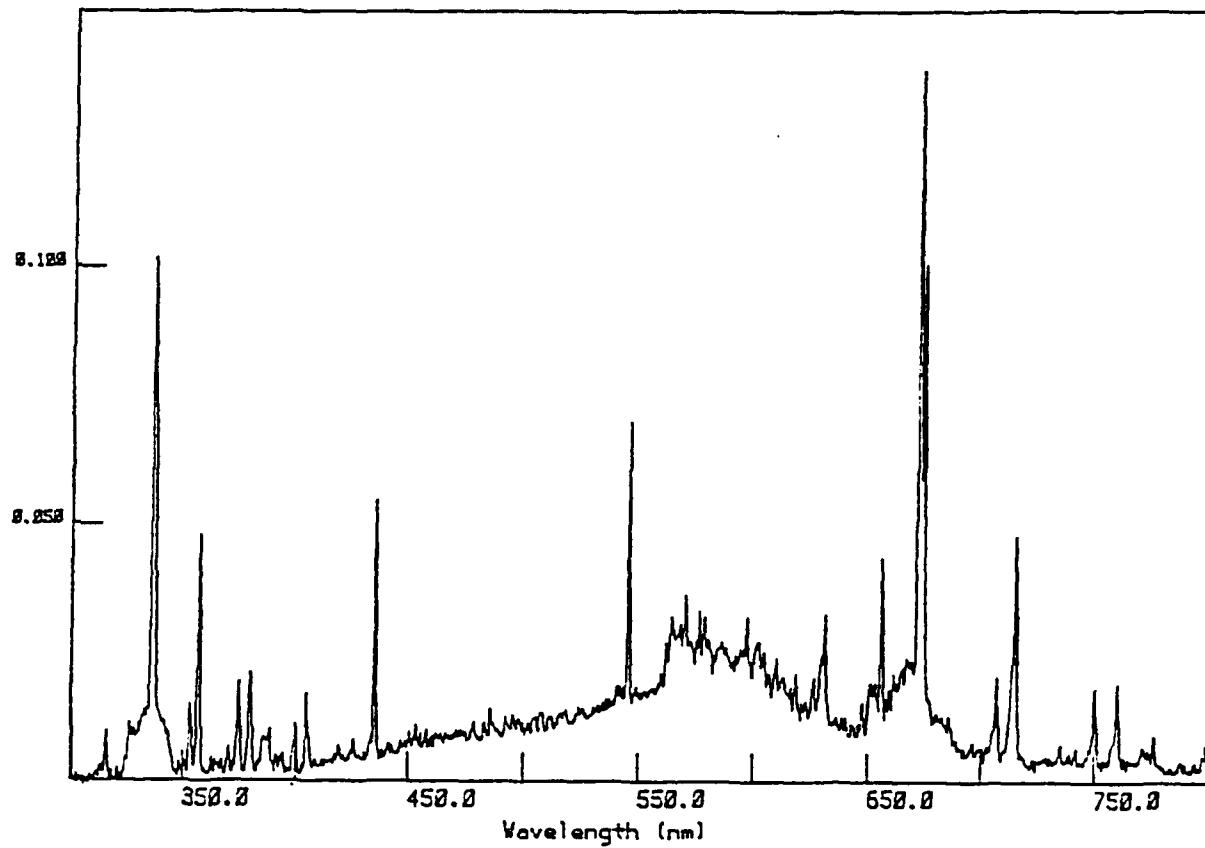


Figure 5. Standard ammonium plasma spectra.

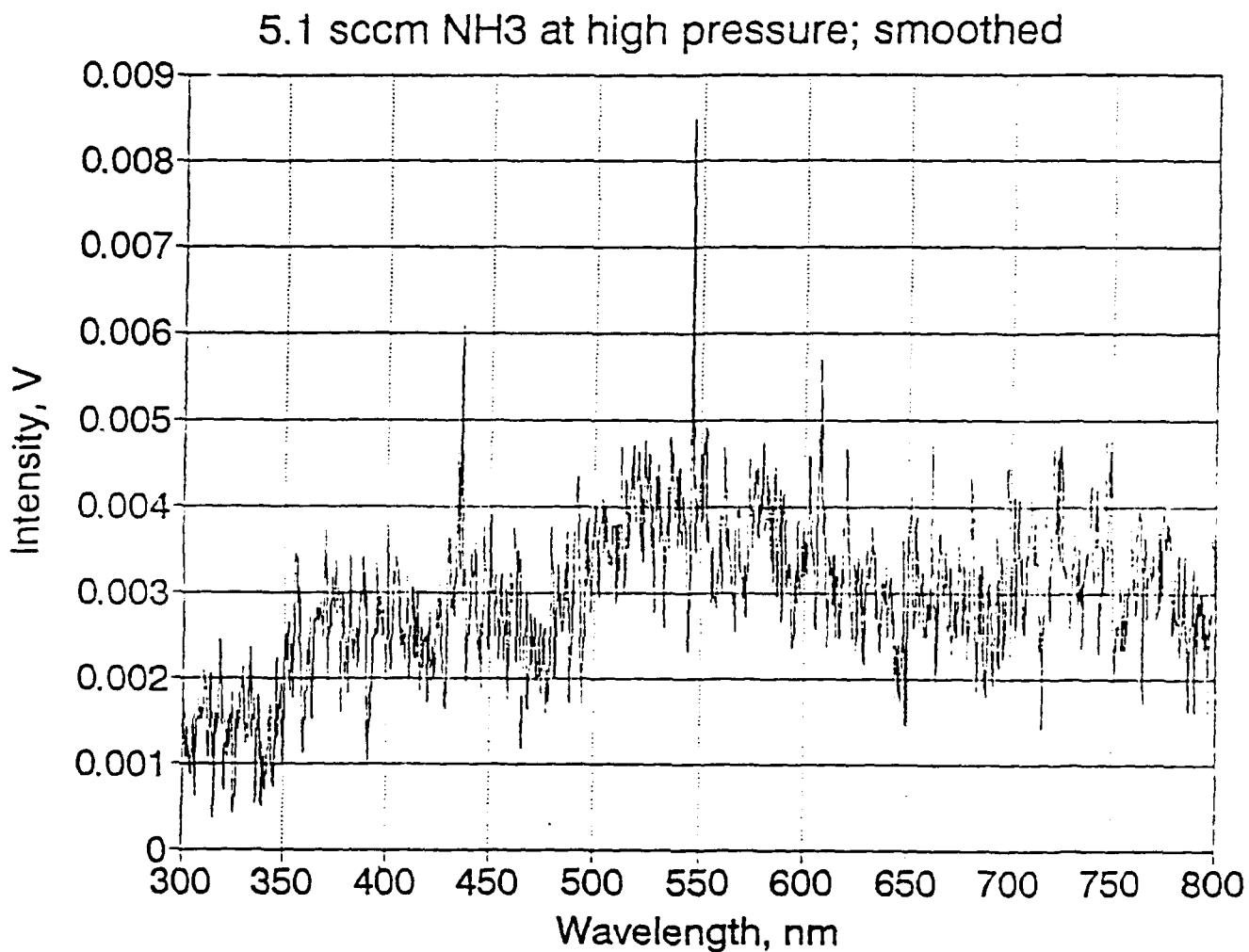


Figure 6. Emission spectra for the plasma delivered to NAWC without fiber present.

Oxygen Plasma

AS4-12K fibers were subjected to the oxygen plasma treatments given in Table II. The net surface acid concentration was measured for each plasma treatment using standard acid and base titration procedures. The net value was obtained by subtracting the total base sites from the total acid sites; negative values indicate base sites.

TABLE II
OXIDATION OF AS4 CARBON FIBERS
WITH AN OXYGEN PLASMA

<u>Plasma Parameters</u>	<u>Net Acid Sites/nm²</u>
1) 50 sccm, 1000 mtorr, 200 W, 60 s	0.785
2) 50 sccm, 1000 mtorr, 200 W, 30 s	-1.140
3) 50 sccm, 1000 mtorr, 200 W, 15 s	1.690
4) 50 sccm, 200 mtorr, 200 W, 15 s	0.900
5) 50 sccm, 200 mtorr, 50 W, 15 s	0.387
6) 50 sccm, 190 mtorr, 50 W, 15 s	-0.017
7) 50 sccm, 190 mtorr, 50 W, 30 s	0.594
8) 50 sccm, 190 mtorr, 50 W, 60 s	-0.319
9) 50 sccm, 190 mtorr, 200 W, 60 s	-0.193
10) 50 sccm, 190 mtorr, 200 W, 30 s	1.279
11) 50 sccm, 190 mtorr, 200 W, 15 s	0.556
12) Untreated	-0.864

Plasma treatment 3 yields the greatest net acid site surface density. For constant gas pressure and power, the shortest plasma treatment time yields higher net acid site surface densities; i.e., treatments 1-3, 7-8, and 9-11. Higher pressures and power levels at equal plasma treatment times yield higher net acid site surface densities; i.e., 6, 5, 11, 4, and 3 in ascending order of net acid site surface densities. These results are intuitive; higher pressures and power levels create more active species that degrade rapidly with time.

The oxygen treated AS4-12K carbon fibers delivered to NAWC were subjected to plasma treatment 3. The emission spectra for this plasma was not taken. The net surface acid concentration was measured to be 1.065 acid sites/nm² using standard acid and base titration procedures. The net value was obtained by subtracting the total base sites from the total acid sites.

Carbon Dioxide Plasma

AS4-12K fibers were subjected to the carbon dioxide plasma treatments given in Table III. The net surface acid concentration was measured for each plasma treatment using standard acid and base titration procedures. The net value was obtained by subtracting the total base sites from the total acid sites; negative values indicate base sites.

TABLE III
OXIDATION OF AS4 CARBON FIBERS
WITH A CARBON DIOXIDE PLASMA

<u>Plasma Parameters</u>	<u>Net Acid Sites/nm²</u>
1) 50 sccm, 75 mtorr, 200 W, 15 s	0.290
2) 50 sccm, 1000 mtorr, 200 W, 15 s	0.951
3) 50 sccm, 125 mtorr, 50 W, 15 s	-0.125
4) 50 sccm, 1000 mtorr, 50 W, 15 s	0.441
5) 50 sccm, 125 mtorr, 50 W, 30 s	0.831
6) 50 sccm, 1000 mtorr, 50 W, 30 s	1.387
7) 50 sccm, 1000 mtorr, 200 W, 30 s	-0.056
8) 50 sccm, 160 mtorr, 200 W, 30 s	0.589
9) 50 sccm, 165 mtorr, 200 W, 60 s	0.456
10) 50 sccm, 1000 mtorr, 200 W, 60 s	1.100
11) 50 sccm, 1000 mtorr, 50 W, 60 s	0.577
12) 50 sccm, 170 mtorr, 50 W, 60 s	0.658
13) Untreated	-1.169

Plasma treatment 6 yields the highest net acid site surface density. Higher pressures at equivalent power and treatment time generally yield more acid sites. There is no consistent correlation between treatment time and power, and acid site surface density. Higher pressures enable a greater number of bimolecular processes to occur. But the plasma chemistry is complex as evidenced by the variations in treatment time and power results.

The carbon dioxide treated AS4-12K carbon fibers delivered to NAWC were subjected to plasma treatment 6. The emission spectra for this plasma was not taken. The net surface acid concentration was measured to be 1.110 acid sites/nm² using standard acid and base titration procedures. The net value was obtained by subtracting the total base sites from the total acid sites. The sample that was subjected to inverse gas chromatography had a net surface acid concentration of 1.253 sites/nm².

Task 3 - Surface Chemical CharacterizationNon-Aqueous Titrations

The density of functional groups induced on the carbon surface by the various plasma treatments was quantified by non-aqueous titrations for total acid and base groups. Basic and acidic groups were quantified by ion-exchange titrations and direct site titrations respectively, using the procedures detailed in "Polymer Preprints," 24, 1, 1983. Direct observation of the plasma gas-phase spectra failed to yield a direct correlation with non-aqueous titration results.

The plasma treated AS4-12K carbon fibers that were delivered to NAWC have measured surface site concentration of 0.169 NH₃ sites/nm², 1.065 acid sites/nm², and 1.110 acid sites/nm² for the optimized ammonia, oxygen, and carbon dioxide plasma treatments, respectively.

ESCA Analysis

Four AS4-12K carbon fibers, an untreated fiber and three fibers subjected to one of the optimized plasma treatments, were submitted to Rocky Mountain Laboratories, Inc. for ESCA analysis. A survey of the relative surface composition was requested. Compositional results for the four fibers are given in Table IV. The ESCA surface survey spectrum and high resolution spectrum (C_{1s}) for the four fibers are given in Figures 7 to 10 and 11 to 14, respectively.

TABLE IV
RELATIVE ELEMENTAL SURFACE COMPOSITION
ON TREATED CARBON FIBERS, [ATOM%]

<u>Sample</u>	<u>C</u>	<u>O</u>	<u>N</u>	<u>Ca</u>	<u>Cl</u>	<u>P</u>	<u>Si</u>	<u>Na</u>
Untreated	87.6	9.0	2.7	0.4	--	0.3	--	--
Ammonia	83.1	10.2	5.1	0.6	0.3	--	0.2	0.4
Oxygen	81.9	14.7	2.1	0.8	--	0.4	--	--
Carbon Dioxide	85.7	11.3	2.2	0.4	--	0.3	0.2	--

ESCA SPECTRUM

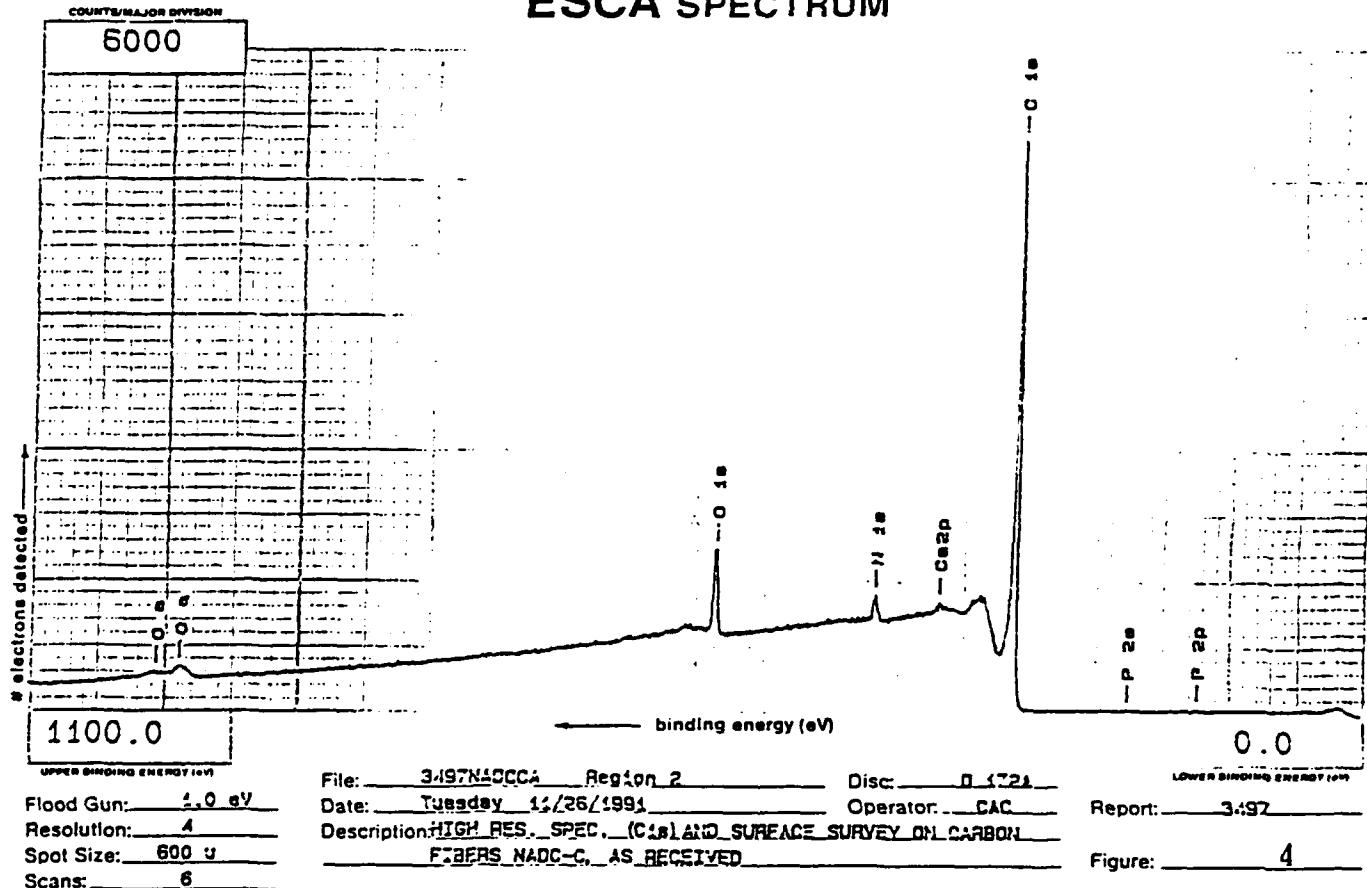


Figure 7. ESCA surface survey of untreated AS4-12K fiber.

ESCA SPECTRUM

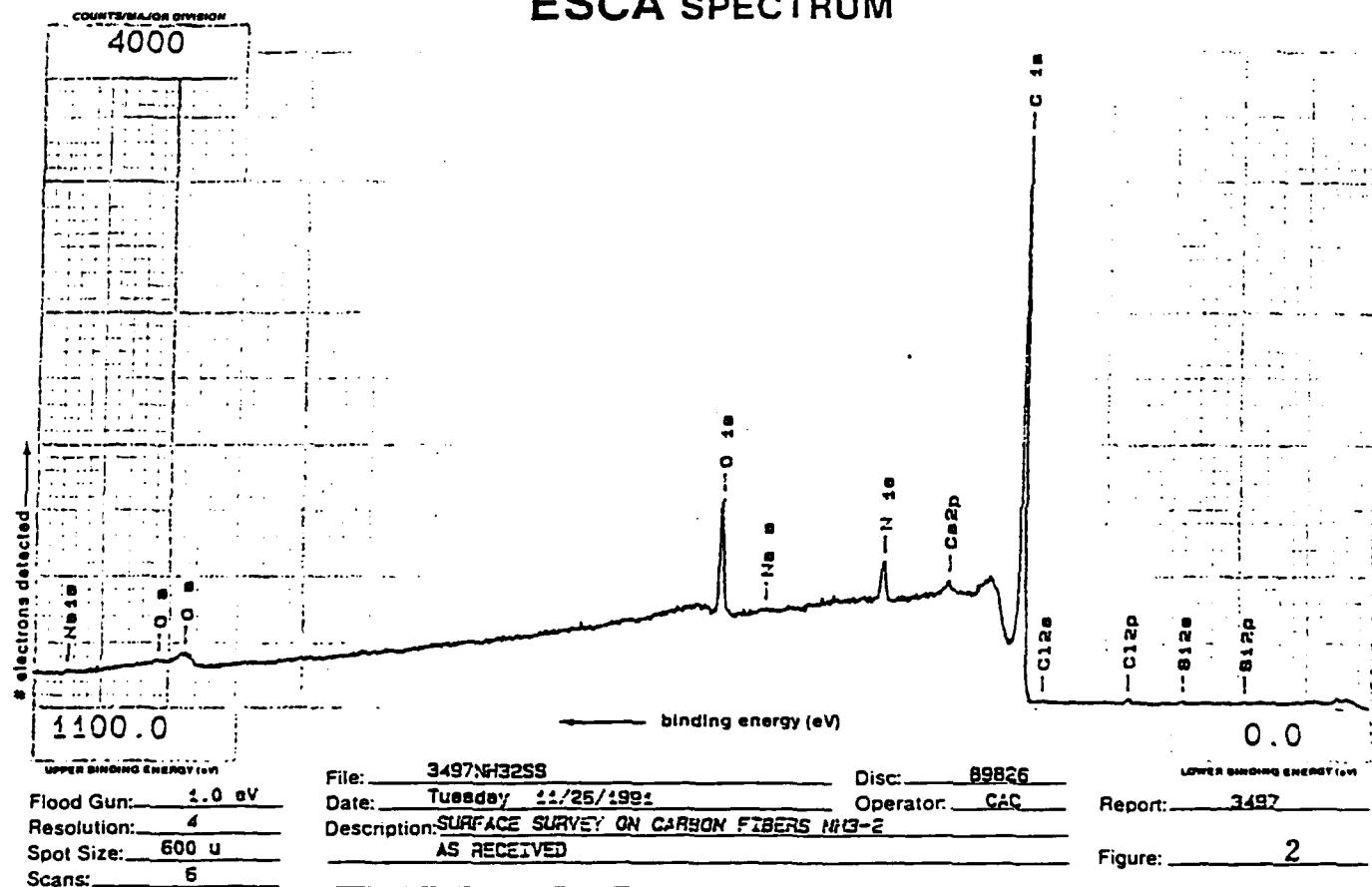


Figure 8. ESCA surface survey of ammonia treated AS4-12K fiber.

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ESCA SPECTRUM

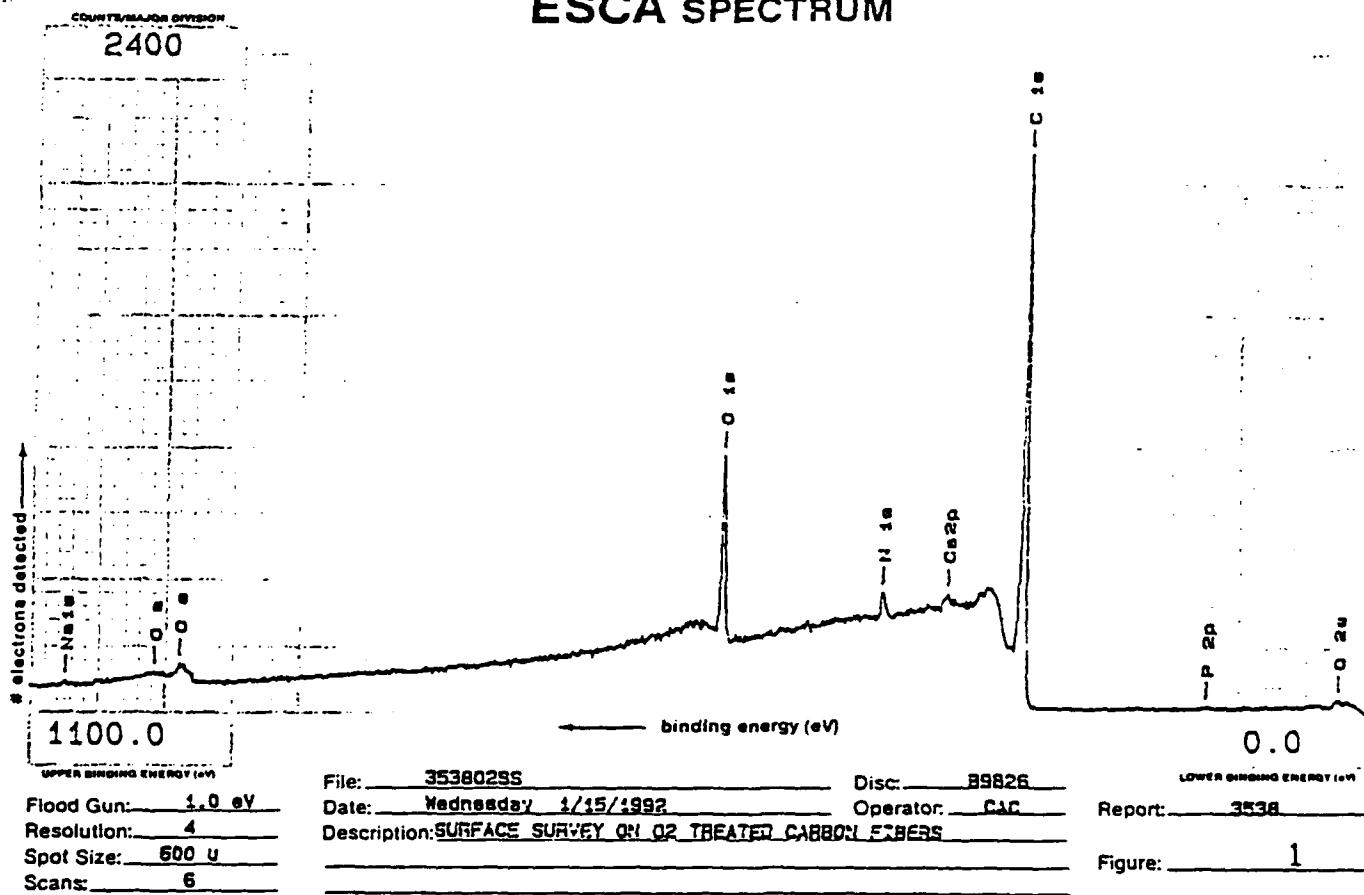


Figure 9. ESCA surface survey of oxygen treated AS4-12K fiber.

ESCA SPECTRUM

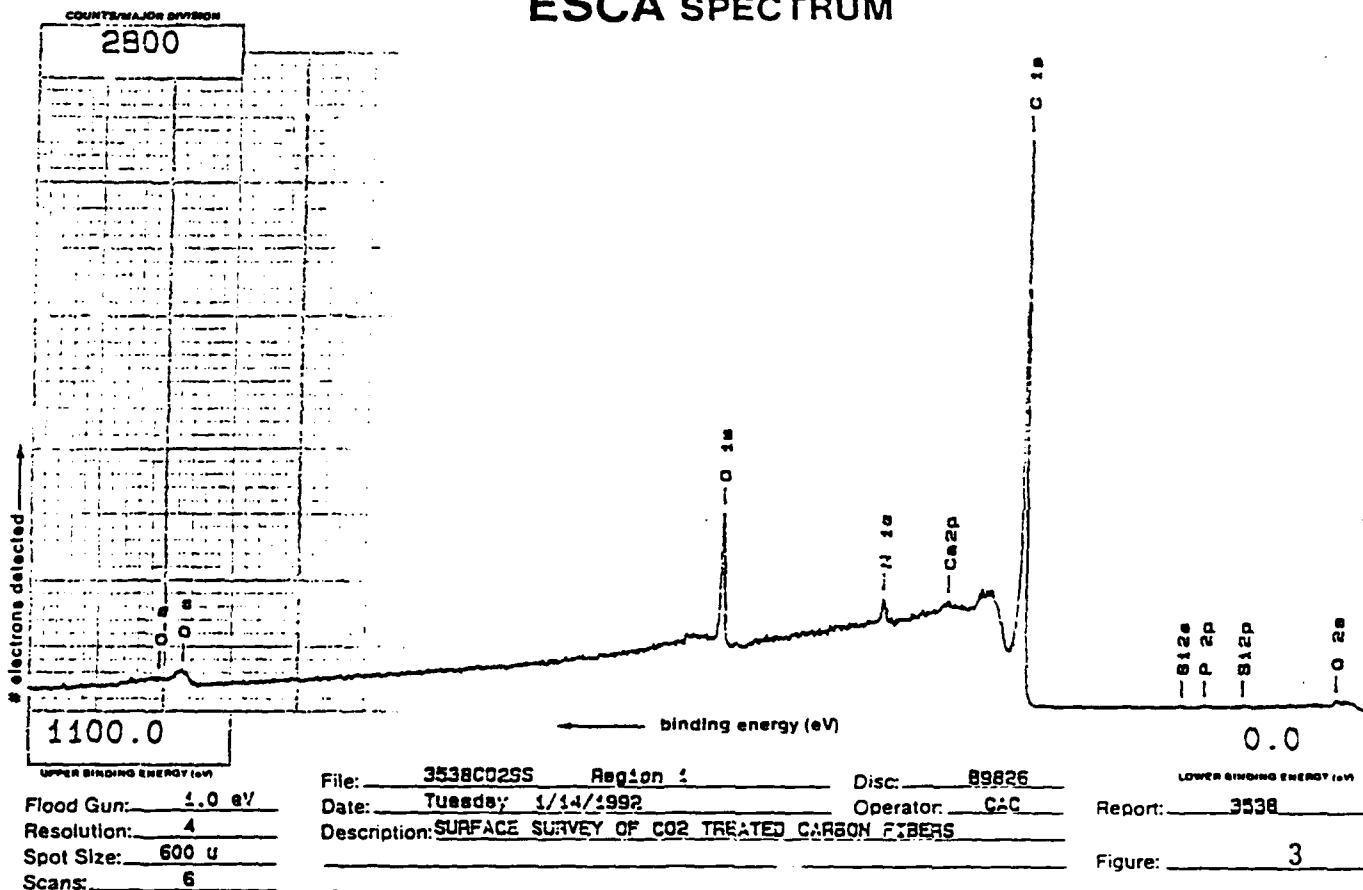


Figure 10. ESCA surface survey of carbon dioxide treated AS4-12K fiber.

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ESCA SPECTRUM

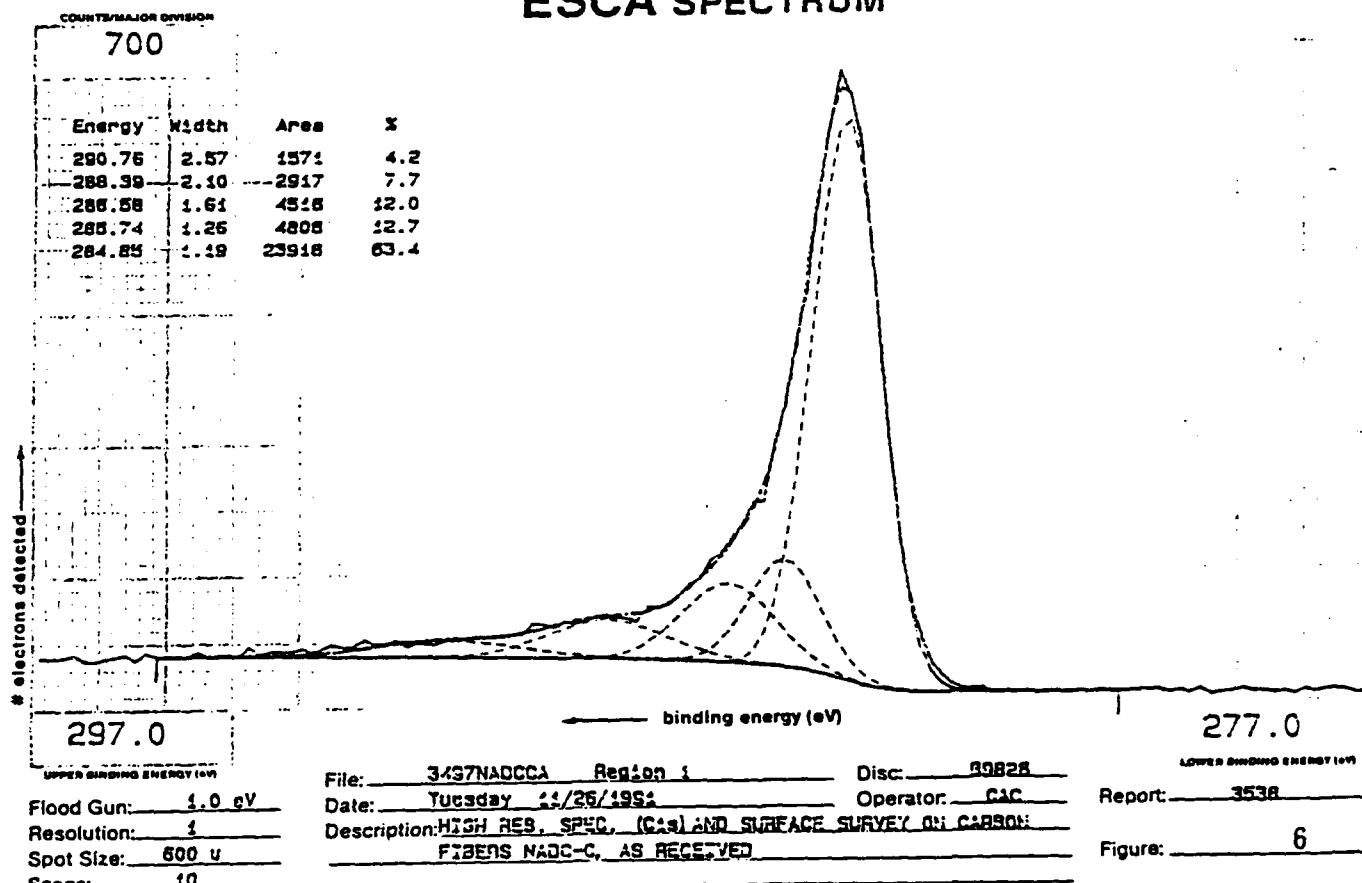


Figure 11. ESCA high resolution spectra (C_{1s}) of untreated AS4-12K fiber.

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ESCA SPECTRUM

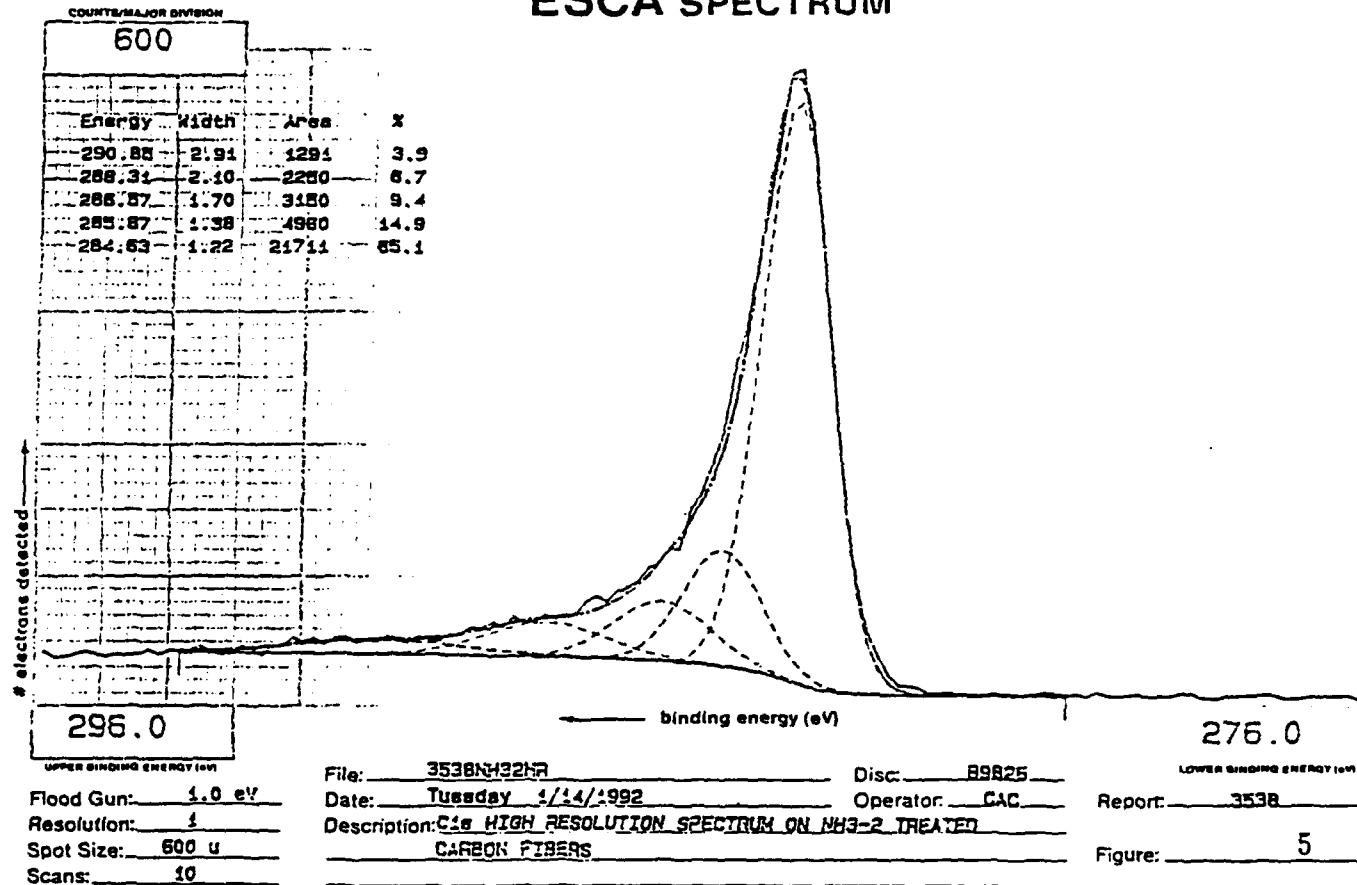


Figure 12. ESCA high resolution spectra (C_{1s}) of ammonia treated AS4-12K fiber.

ESCA SPECTRUM

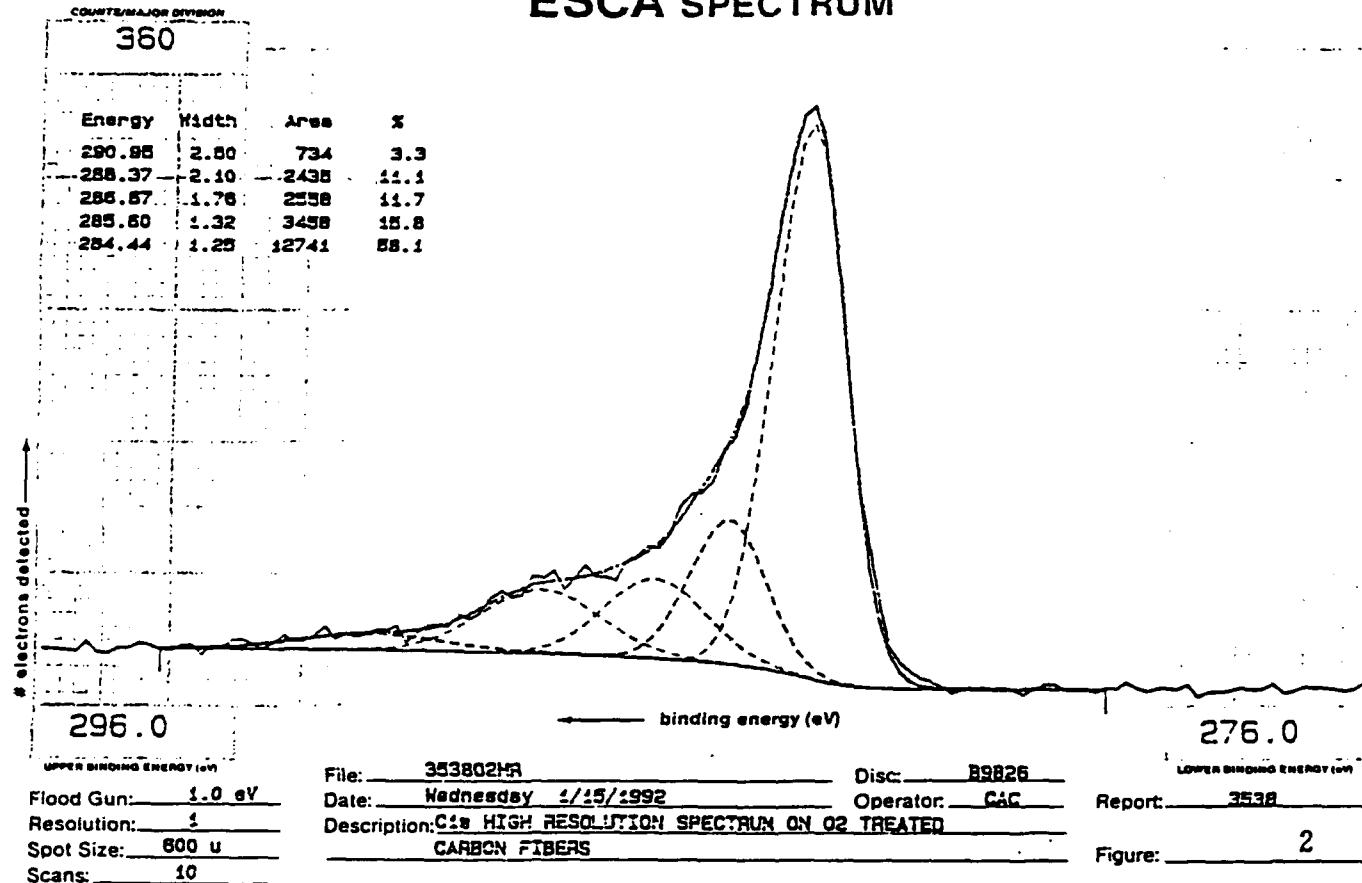


Figure 13. ESCA high resolution spectra (C_{1s}) of oxygen treated AS4-12K fiber.

ESCA SPECTRUM

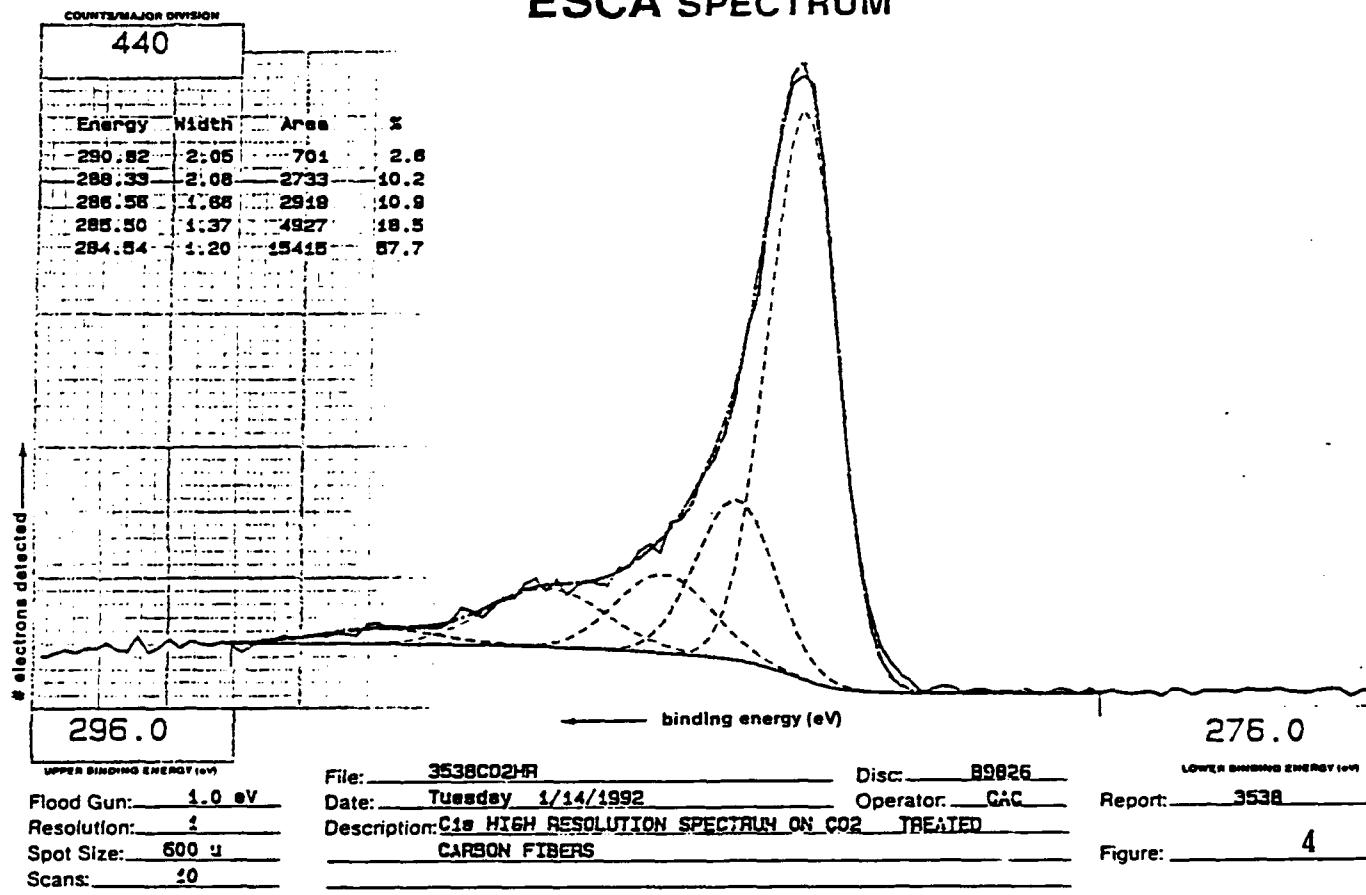


Figure 14. ESCA high resolution spectra (C_{1s}) of carbon dioxide treated AS4-12K fiber.

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The relative abundances of carbon species on the surface of treated carbon fibers, atom %, as determined by ESCA high resolution (C_{1s}) spectra are given in Table V. The explanation of symbols used in Table V are given in Table VI.

TABLE V

RELATIVE ABUNDANCES OF CARBON SPECIES ON THE SURFACE
OF TREATED CARBON FIBERS, [ATOM %]

Symbol	C_1	C_2	C_3	C_4	C_5
Binding Energy ± 0.3 eV	284.6	285.6	286.6	288.4	290.8
Untreated	63.4	12.7	12.0	7.7	4.2
Ammonia	65.1	14.9	9.4	6.7	3.9
Oxygen	58.1	15.8	11.7	11.1	3.3
Carbon Dioxide	57.7	18.5	10.9	10.2	2.6

TABLE VI

EXPLANATION OF SYMBOLS USED IN TABLE V

Symbol	B. E. ± 0.3 eV	Possible Chemical Species
C_1	284.6	"hydrocarbon," graphite, C-C, C=C, C≡C
C_2	285.6	" β -shifted carbon," R_3C-NR_2 , $R-CO-NH-CR_3$
C_3	286.6	R_3C-OH , $R_3C-O-CR_3$, $RCO-OCR_3$
C_4	288.4	$R-CO-O-CR_3$, $R-CO-OH$
C_5	290.8	$RO-CO-OR$, aromatic shake-up

High resolution ESCA spectra indicate that the graphite surface is attacked and converted to esters and/or carboxylic acid moieties (the high energy C_4 peak is 50 percent greater) for the oxygen and carbon dioxide plasma treated fibers.

Inverse Gas Chromatography

The surface acidity and basicity of plasma treated carbon fibers was evaluated by inverse gas chromatography (IGC) and programmed thermal desorption (PTD). Adsorption isotherms computed from chromatograms show changes in weak to medium strength surface sites resulting from treatment, while PTD provides an empirical index of the chemisorptive capacity of the surfaces. These analytical techniques provide another quantification of the acid-base character of AS4 carbon fiber subjected to ammonia, oxygen, and carbon dioxide plasmas, and compares these properties with those of the untreated and commercially oxidized AS4 fiber.

Experimental

Measurements were conducted at TRI in Princeton, NJ by Dr. Sheldon P. Wesson. Data were obtained with an Hewlett-Packard 5890 Series II gas chromatograph fitted with a flame ionization detector (FID) and an RS232C interface board (HP option # 560). The serial interface provides 31 bit resolution of full scale FID current at a maximum collection rate of 20 Hz. An IBM AT compatible computer connected to the interface through a serial port was programmed in ASYST to collect FID output, and to interrogate and control all of the operating parameters of the chromatograph.

IGC: The procedure for loading chromatographic columns with carbon fiber was described previously [1, 2]. Nickel columns 6.4 mm o.d., 5.3 mm i.d. and 55 cm in length were loaded with 5 g samples of fiber to provide about 1 m² of surface area for analysis. Injector and detector temperatures were maintained at 150 and 200°C, respectively. Helium carrier flow rates were measured with a Gasmet flow meter and were maintained at 30 ml/min. Gas holdup times were measured with 20 µl injections of methane.

Hamilton 7101NCH syringes were used to inject 2 µl volumes of pentane (neutral probe) and t-butylamine (Lewis base); injections of t-butanol (Lewis acid) were restricted to 0.5 µl in order to obtain sharp peak fronts. The method for transforming diffuse profiles into adsorption isotherms was described previously [1, 2]. The geometric specific surface $\Sigma_{geo} = 4/pd$ was computed for each fiber sample using measured values for diameter and manufacturers specifications for density. Adsorption volume n (µmoles/g) was normalized for Σ_{geo} so that isotherms are displayed as n/Σ_{geo} (µmoles/m²) versus equilibrium pressure in kPa.

PTD: A column newly loaded with carbon fiber was placed in the chromatograph and conditioned for 2 hours at 30°C under a helium carrier flow of 30 cc/min. 2 µl of t-butylamine was then injected onto the column with a Hamilton 7000.5 NCH syringe, and the resultant chromatogram (FID detector units vs. time since injection) was monitored at 30°C until the FID signal declined from $2 \cdot 10^8$ detector units at peak maximum to an arbitrary level of $2 \cdot 10^4$

detector units. Signals from the FID and oven thermometer were collected every 0.25°C as columns were subjected to a linear temperature increase (ramping) from 30 to 300°C at 5°C per minute. Chromatograph setpoints were entered as follows: initial temperature, 30°C; initial time, 0.1 minutes; program rate, 5°C per minute; final temperature, 300°C; final time, 0.1 minutes. Thermal desorption polytherms are presented as detector units normalized for the geometric surface area in the column (DU/m²) versus column temperature. The method was described previously [2].

Materials: A full bobbin of untreated AS4-12K carbon fiber and 100 g bobbins of AS4-12K fiber treated with ammonia, oxygen and carbon dioxide plasmas were obtained from TPL Inc., Albuquerque, NM. This fiber is termed XAS4-12K in the Figures in this section to differentiate it from non-TPL fibers.

Samples of air plasma treated AS4-12K fiber were obtained from Dr. Theodore Davidson of Stevens Polytechnic Institute in the course of a separate study. Conditions of treatment are given as 1.4 torr pressure, 80 W forward/50 W back plasma power, and 30 minutes glow time in a batch mode reactor. Samples of standard electrooxidized AS4 carbon fiber were obtained periodically from Hercules, Inc. and analyzed at TRI over a period of five years.

Results and Discussion

The sorptive capacity of a substrate may change because surface energetics and specific surface are modified simultaneously. Changes in surface acid-base character will not affect adsorption of a probe that interacts by dispersion forces only. Figure 15 shows monolayer pentane adsorption on AS4 carbon fiber before and after plasma treatment. Changes in pentane isotherms are caused only by modification of specific surface, and the near registry of all the pentane isotherms indicate that plasma treatment does not affect the surface rugosity on a scale that can be detected by molecules with the effective molecular area of pentane. The inference is that changes in surface energetics can be displayed by normalizing the adsorption volume by the geometric specific surface of these samples.

Monolayer isotherms for t-butylamine on AS4 fiber before and after plasma treatment are displayed in Figure 16. Replicate measurements are shown for each sample to display the experimental precision of the method, which entails loading the column with new fiber after each measurement. The sample-to-sample precision is sufficient to demonstrate that the sorptive capacity for the basic probe of fiber treated with O₂ and CO₂ plasma is greater than that of the control across the entire pressure range. NH₃ plasma has no appreciable effect on the sorptive capacity of carbon fiber for the basic probe. The inference is that the plasmas containing oxygen are efficacious at implanting surface acidity on carbon fiber surfaces.

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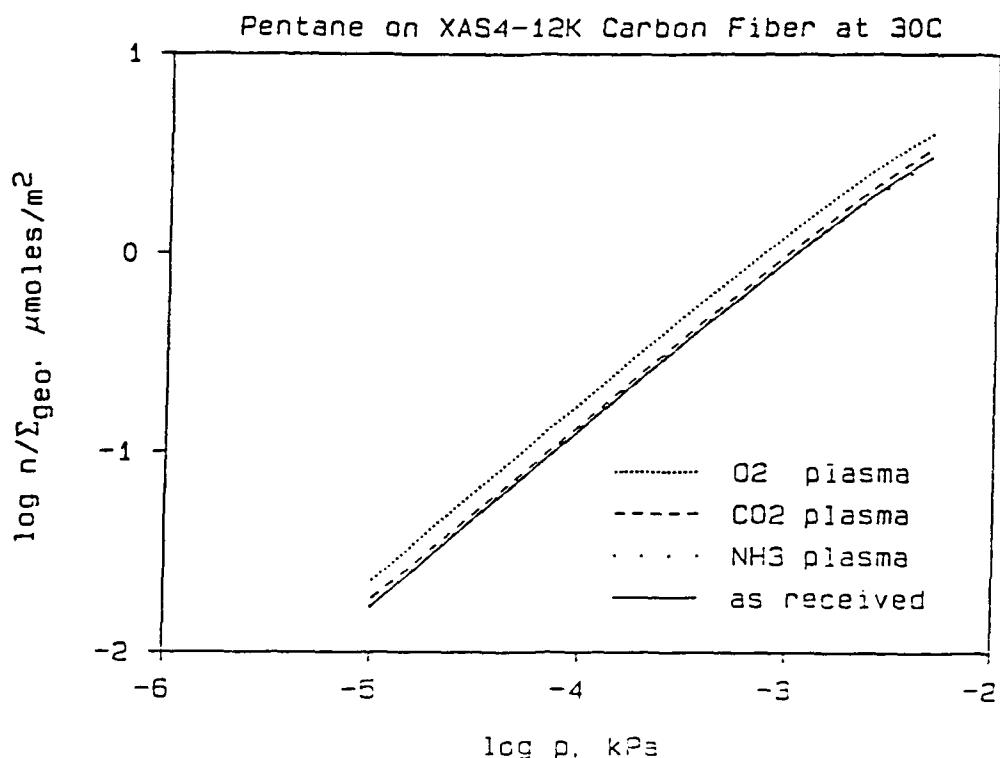


Figure 15. Pentane on XAS4-12K carbon fiber at 30°C.

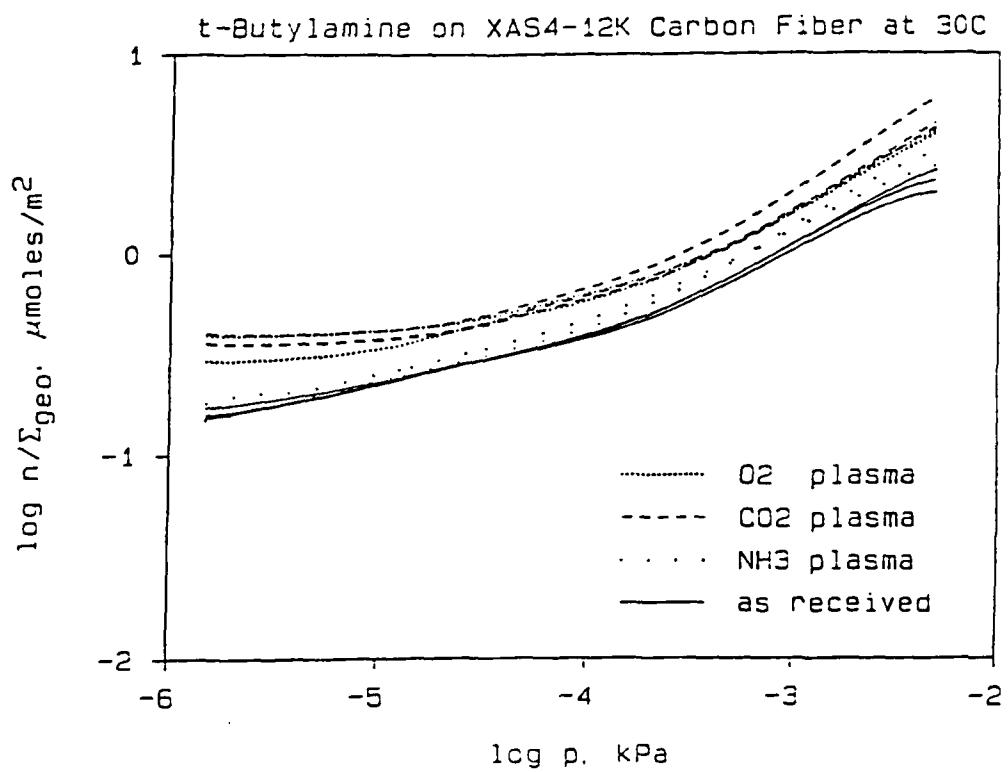


Figure 16. t-Butylamine on XAS4-12K carbon fiber at 30°C.

The thermal stability of acidic functionality on carbon fiber surfaces is of interest. Figures 17 and 18 show that the surface acidity of control and plasma treated fiber is equivalent before and after ramping from 30°C to 300°C. Physical adsorption isotherms measure dispersion force interactions and weak acid-base attraction; the inference is that weakly acidic sites are not affected by this thermal treatment.

Carbon fiber surfaces feature adventitiously adsorbed organic contaminants. Previous work shows that carbon fiber is an effective getter for ambient organics. Figure 19 shows that AS4 fiber shows a significant desorption polytherm above 100°C consisting of organic contaminants. Plasma treatments scrub some of this material from the surface; ramping removes it almost completely. Since the surface energetics of the fiber as revealed by monolayer adsorption is invariant with ramping, one inference is that weakly acidic surface sites are not covered by organic contaminants.

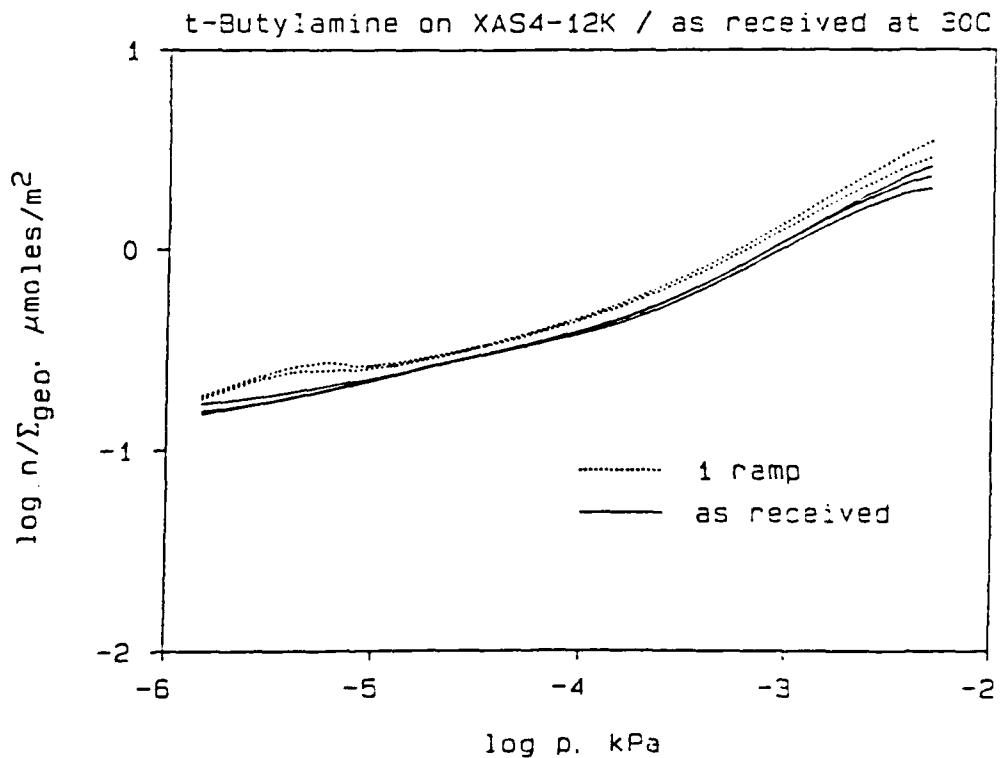


Figure 17. t-Butylamine on XAS4-12K as received at 30°C.

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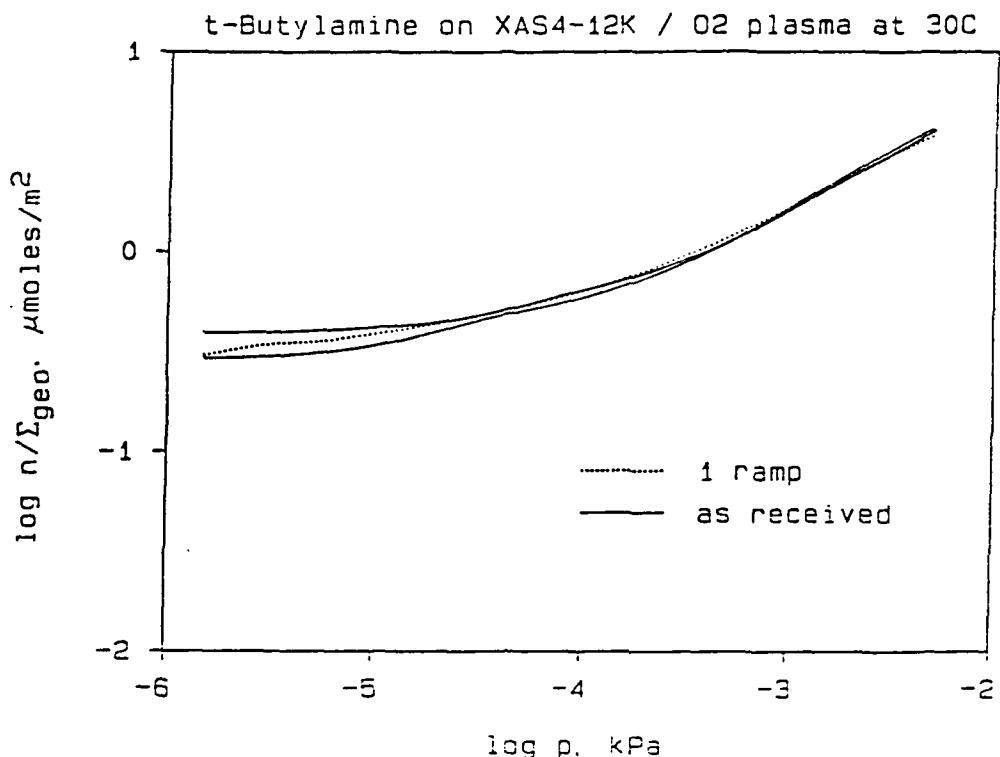


Figure 18. t-Butylamine on XAS4-12K oxygen plasma at 30°C.

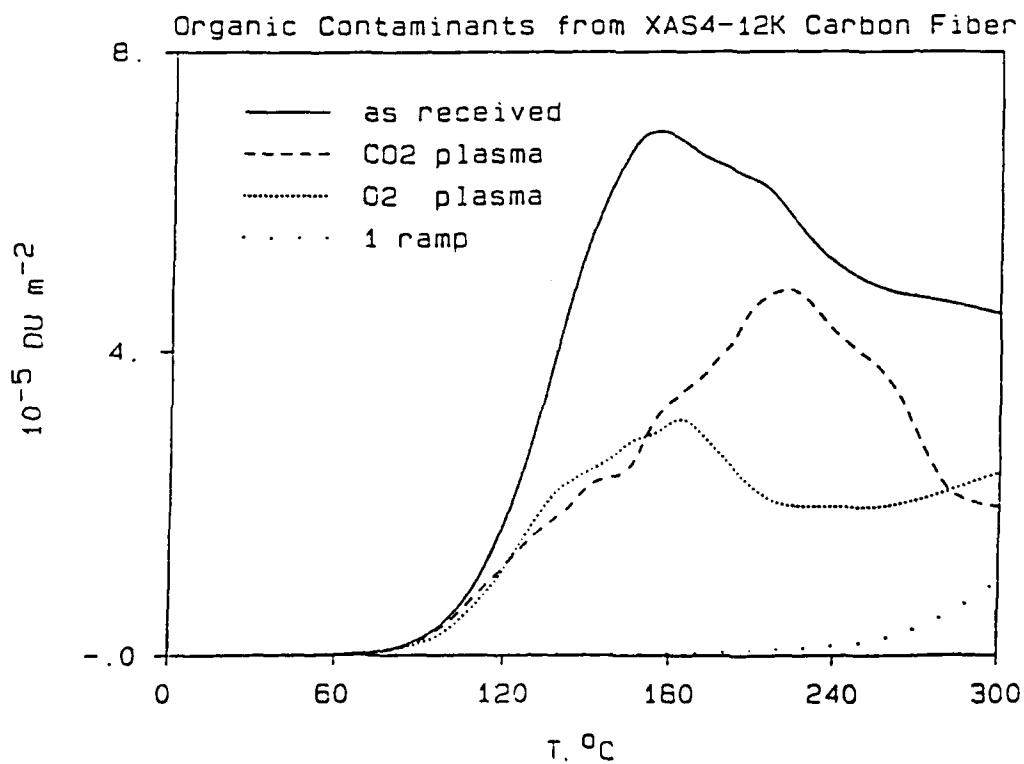


Figure 19. Organic contaminants from XAS4-12K carbon fiber.

Figure 20 shows t-butylamine isotherms on different lots of AS4 carbon fiber manufactured over a period of several years. These isotherms are similar but not identical considering the precision of the method. Figure 21 shows that O₂ and CO₂ plasma treatment augments carbon fiber surface acidity, and to a greater extent than that can be expected from lot-to-lot variation in carbon fiber manufacture.

Results of monolayer adsorption analysis can be quantified by treating the data with a model that delivers an adsorption energy distribution for the substrate. Figures 22 and 23 show distributions resulting from analysis of adsorption on control and O₂ plasma treated AS4 fiber. Both are bimodal, with most of the surface in the low energy sector of the adsorption energy range. The important difference is the surface fraction of high energy sites, which increases significantly upon plasma treatment. The surface fraction of high energy sites from t-butylamine adsorption for each fiber specimen is listed as $\Sigma_{\text{chemisorption}}$ in Table VII.

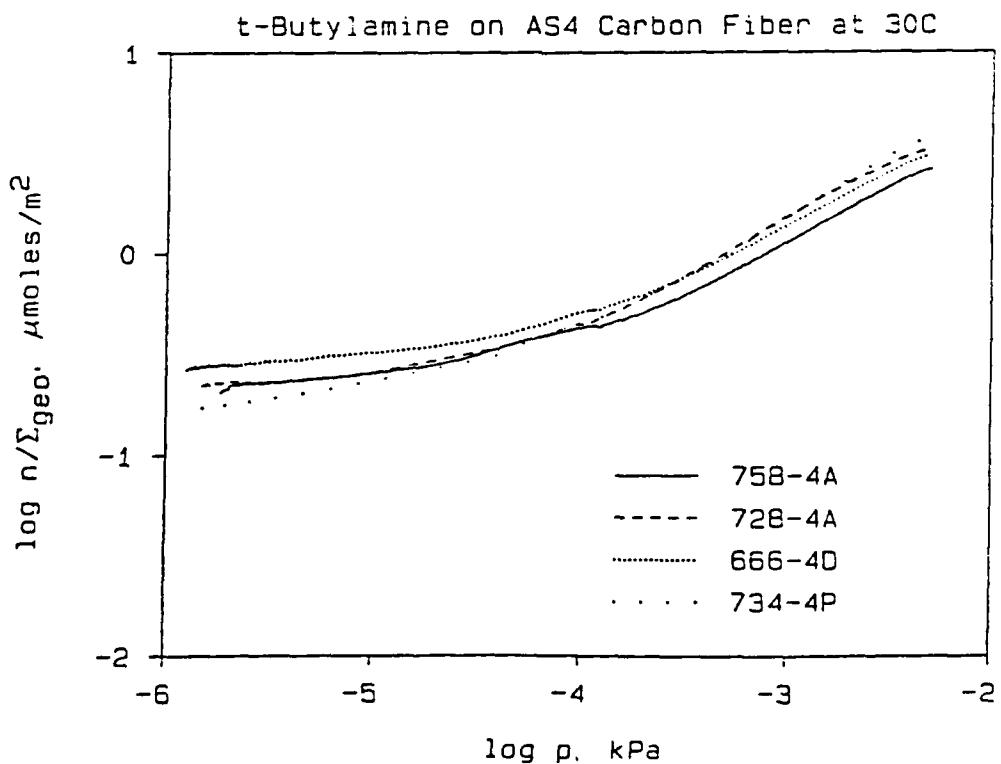


Figure 20. t-Butylamine on AS4 carbon fiber at 30°C.

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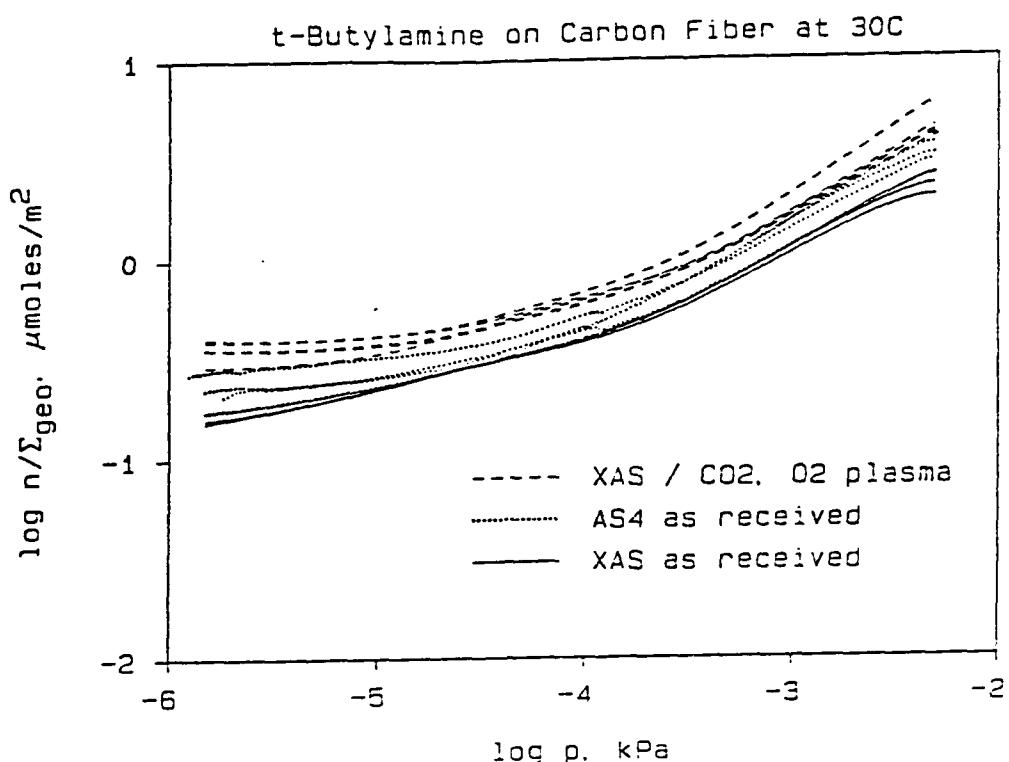


Figure 21. t-Butylamine on carbon fiber at 30°C.

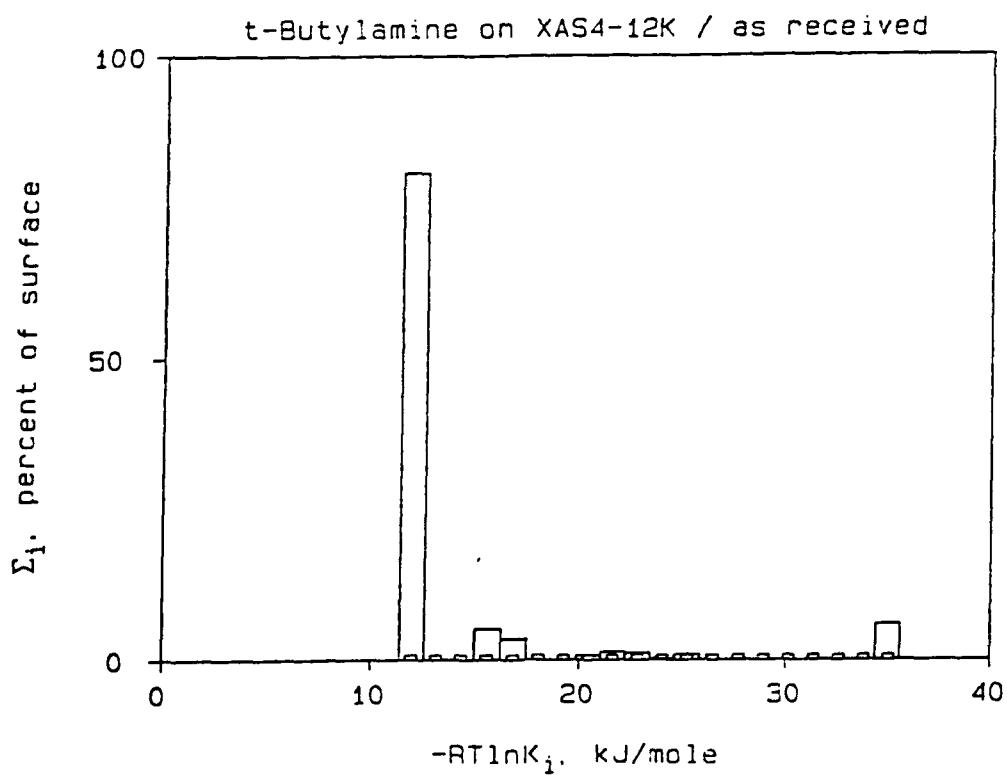


Figure 22. t-Butylamine on XAS4-12K as received.

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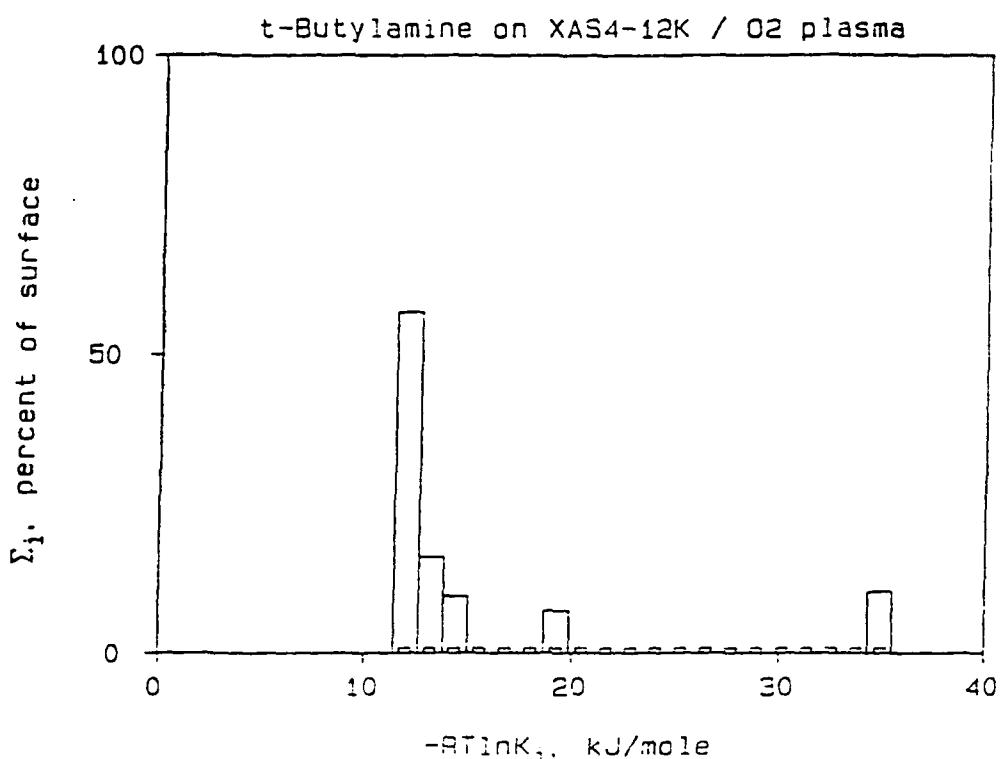


Figure 23. t-Butylamine on XAS4-12K oxygen plasma.

Analysis of monolayer isotherms shows changes in surface concentrations of weak and moderately strong acid and basic sites (physisorption). Stronger acid-base interactions (chemisorption) are characterized by programmed thermal desorption, by which the minute residue of probe remaining on the surface after the chromatogram is obtained is driven off by ramping the system temperature.

FID response is proportional to the total concentration of organic material in the carrier stream: the PTD curve obtained when probe desorbs from carbon fiber is therefore a composite of extraneous organics desorbed from the column wall, probe desorbed from the column wall, extraneous organics desorbed from the carbon fiber, and probe desorbed from the fiber surface. Our protocol therefore consists of subtracting the first three quantities from the total PTD envelope to obtain the quantity of interest, the probe desorbed from the fiber surface.

Figure 24 shows three families of curves obtained by ramping AS4 fiber as received. Family 1 consists of replicate measurements of FID output (dotted curves) as fiber was ramped from 30°C to 300°C in the chromatographic column. The average curve obtained from replicate measurements is represented by the solid line. Families 2 and 3 result from obtaining chromatograms with t-butanol and t-butylamine, respectively, prior to ramping.

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TABLE VII. t-BUTYLAMINE ON CARBON FIBER

<u>IGC</u>	$\Sigma_{\text{chemisorption}} (\%)$	
AS4 / as received	6.0	
AS4 / NH ₃ plasma	4.3	
AS4 / CO ₂ plasma	10.6	
AS4 / O ₂ plasma	10.3	
<u>PDT</u>	Volume Desorbed (10^{-5} DU $^{\circ}\text{C}/\text{m}^2$)	T_{\max} ($^{\circ}\text{C}$)
AS4 / as received	52.0	70
1 ramp	42.7	75
AS4 / NH ₃ plasma	43.3	70
	49.3	75
AS4 / CO ₂ plasma	76.6	70
	56.5	75
XAS4 / O ₂ plasma	75.9	70
	73.8	75
AS4 / air plasma	58.0	70

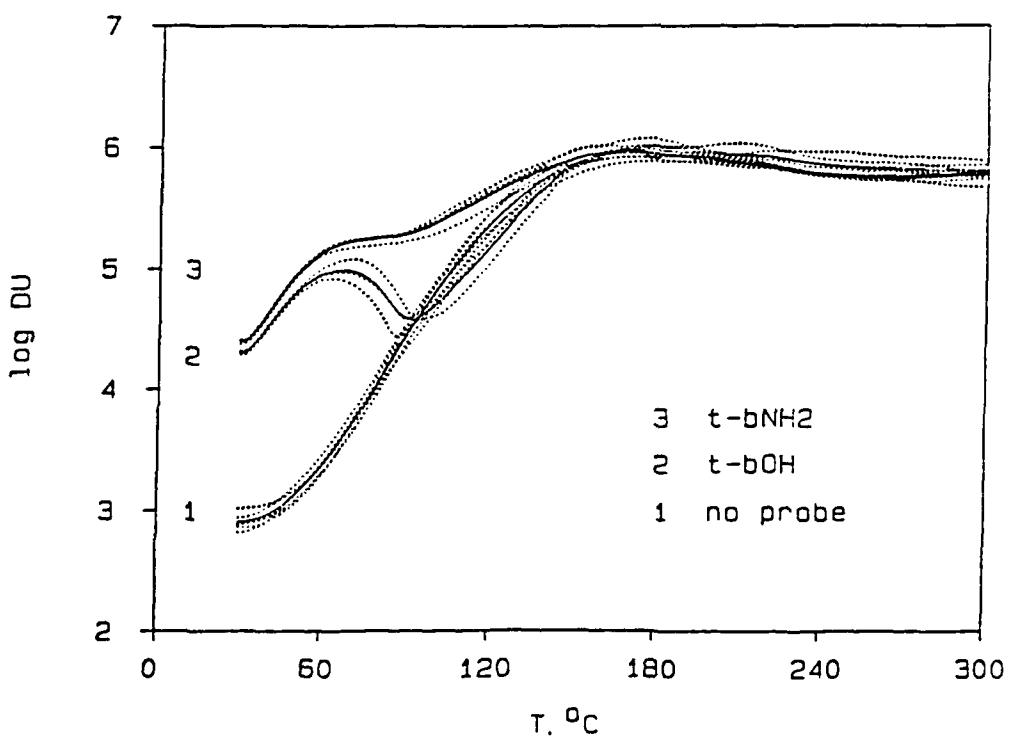


Figure 24. Desorption from XAS4-12K as received.

The process of subtracting all the extraneous contributions from the total desorption envelope is shown in Figure 25, which shows PTD curves as detector units normalized for the total surface area in the column. The dotted line in Figure 19 shows desorption of probe and contaminants (the solid curve in Figure 24, family 3). The dashed line shows desorption of contaminants alone from a column of fiber which was not injected with probe (the solid curve in Figure 24, family 1). The solid curve results from subtracting the dashed curve from the dotted curve, and therefore displays t-butylamine desorbed from the carbon fiber surface with all extraneous desorption subtracted out. This quantity is taken as an index of the chemisorptive capacity of the substrate for the probe.

Figures 26 and 27 display the same process for analyzing the chemisorptive capacity of AS4 fiber after O₂ plasma treatment. Comparison with Figures 24 and 25 readily shows that the combined effect of surface contaminant removal and augmenting surface acidity by the plasma extends the effective range of PTD analysis from 200°C (Figure 25) to nearly 300°C (Figure 27).

Subtraction polytherms from all AS4 samples consisting of data replicated and averaged as described above is displayed in Figure 28. It is readily apparent that O₂ and CO₂ plasmas augment the chemisorptive capacity of AS4 fiber for the basic probe dramatically, while polytherms for fiber as received and NH₃ plasma treated are essentially equivalent. These peaks are a complex combination of many components; we have presented a detailed discussion about these envelopes previously [2]. Our interpretation is that features in the polytherm below 100°C constitute an index of surface acidity, and features in the high temperature sector of the polytherm may be indicative of surface damage. These results are numerically summarized in Table VII by integrating under the polytherm between 30°C and the first maximum at 70°C, and presenting twice that value as the desorption volume of the first constituent peak.

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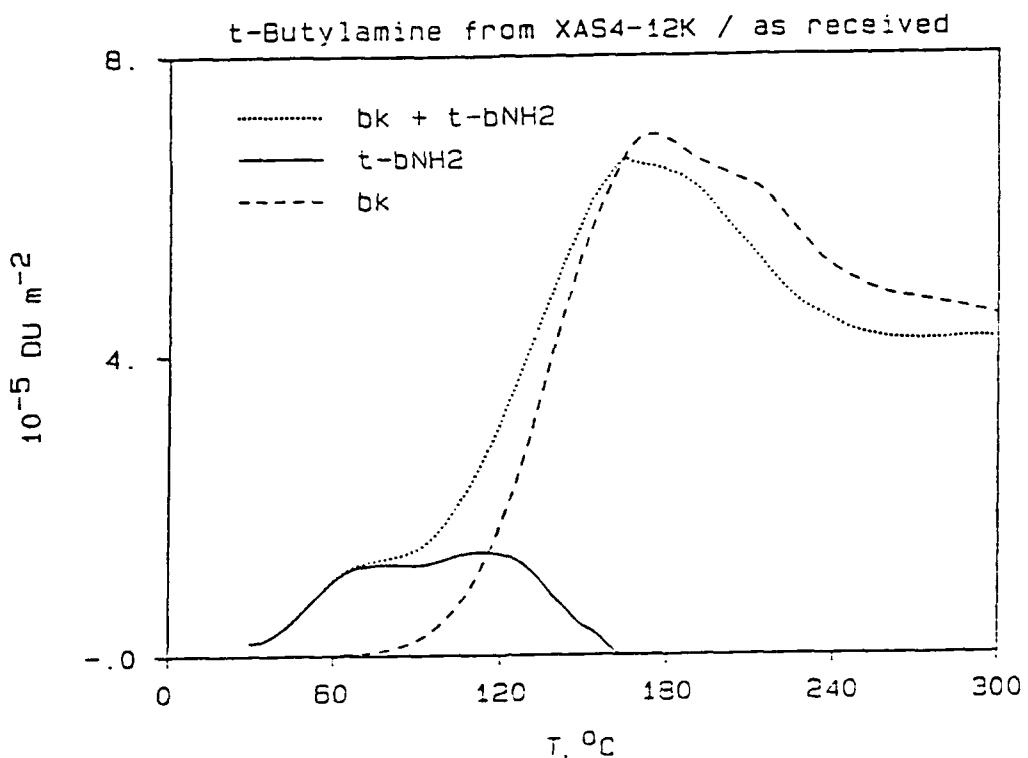


Figure 25. t-Butylamine from XAS4-12K as received.

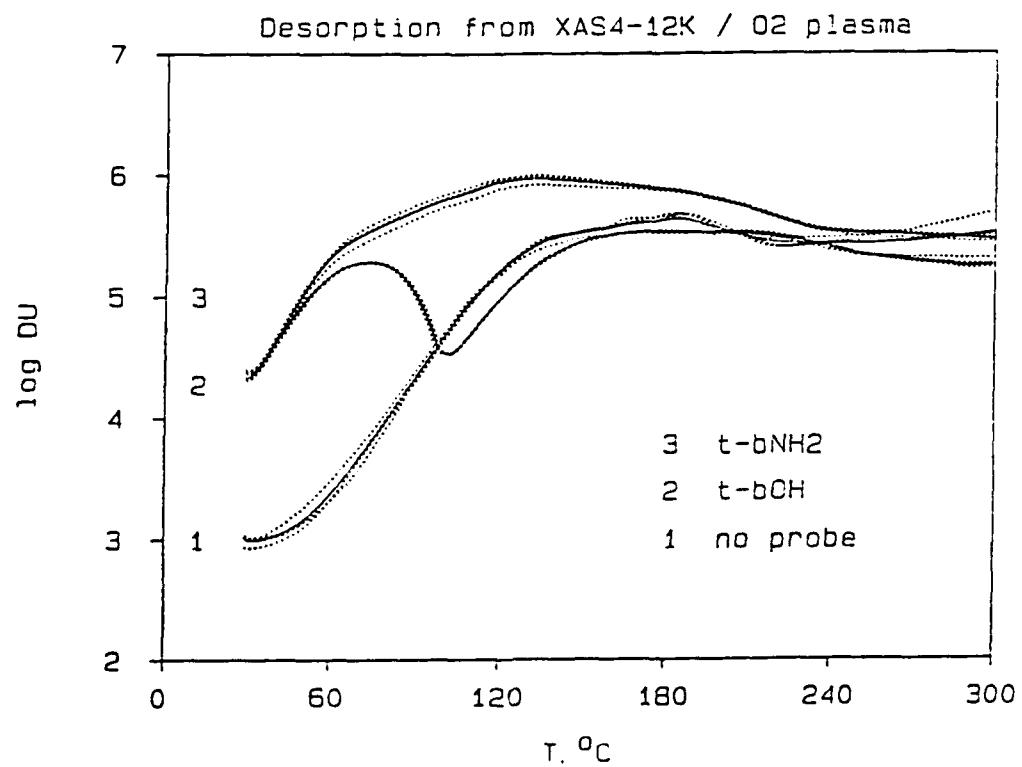


Figure 26. Desorption from XAS4-12K oxygen plasma.

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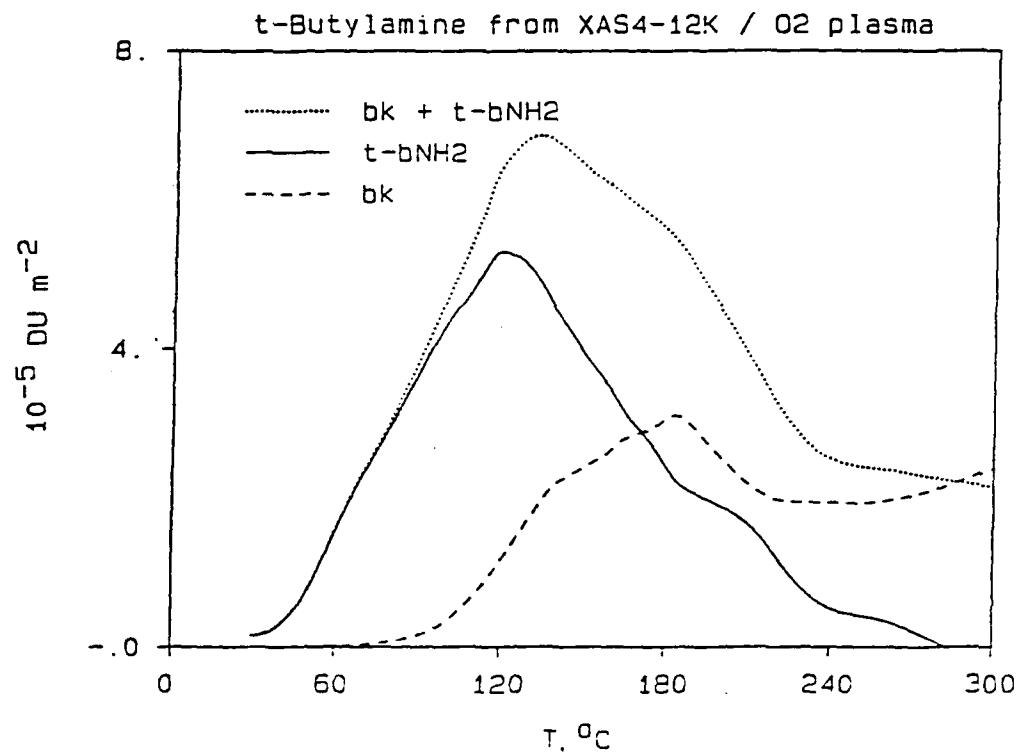


Figure 27. t-Butylamine from XAS4-12K oxygen plasma.

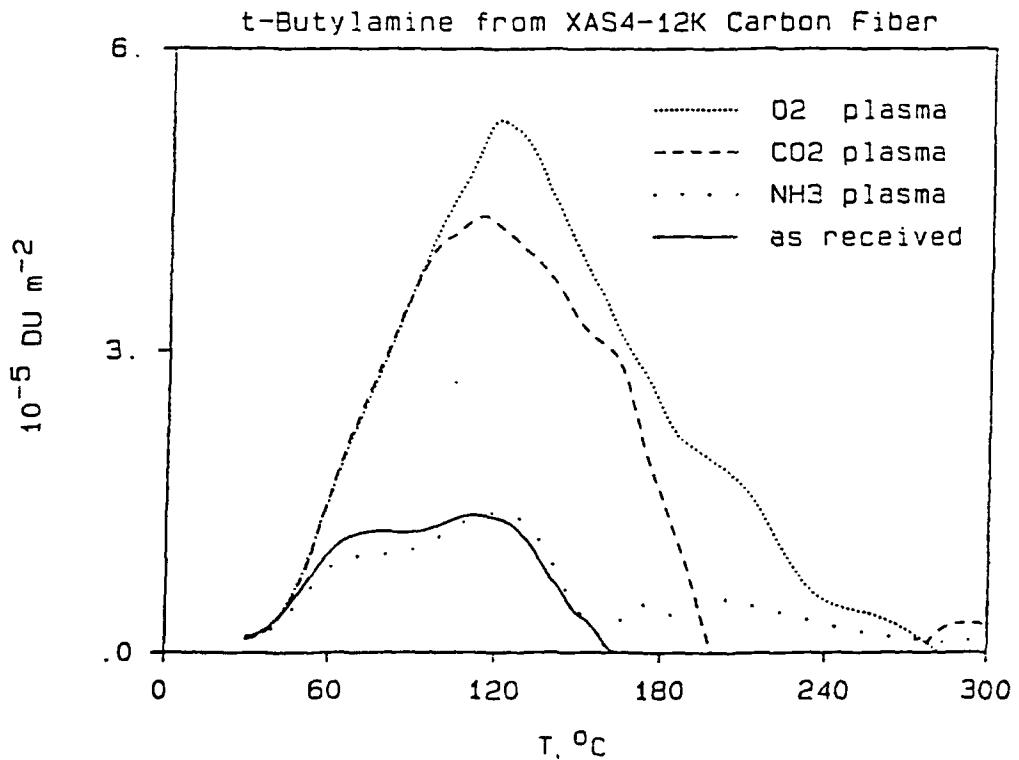


Figure 28. t-Butylamine from XAS4-12K carbon fiber.

Figure 29 displays polytherms obtained on fiber samples after one ramp. The high temperature sector of polytherms in Figure 28 are nearly obliterated by thermal treatment; the low temperature peak is affected less. The same integration procedure is used to tabulate the desorption volume from thermally treated samples. It is interesting to note that, after ramping, plasma treated samples remain more acidic than the control, according to our protocol.

Figure 30 presents chemisorption polytherms obtained from historical AS4 samples. It is apparent from Figure 31 that plasma treatment augments the chemisorptive capacity considerably beyond that expected from lot-to-lot variation.

Polytherms showing the effect of various oxidative plasmas on surface acidity are shown in Figure 32. Peak shapes of O₂, CO₂ and XAl plasmas are similar across the temperature range, and identical up to 100°C. The chemisorption envelope from air plasma treatment is significantly different, however. This envelope is not substantially greater than that of control fiber in the low temperature sector; one inference is that air plasma treatment causes an equivalent degree of surface damage as the other treatments, while imparting less surface acid functionality.

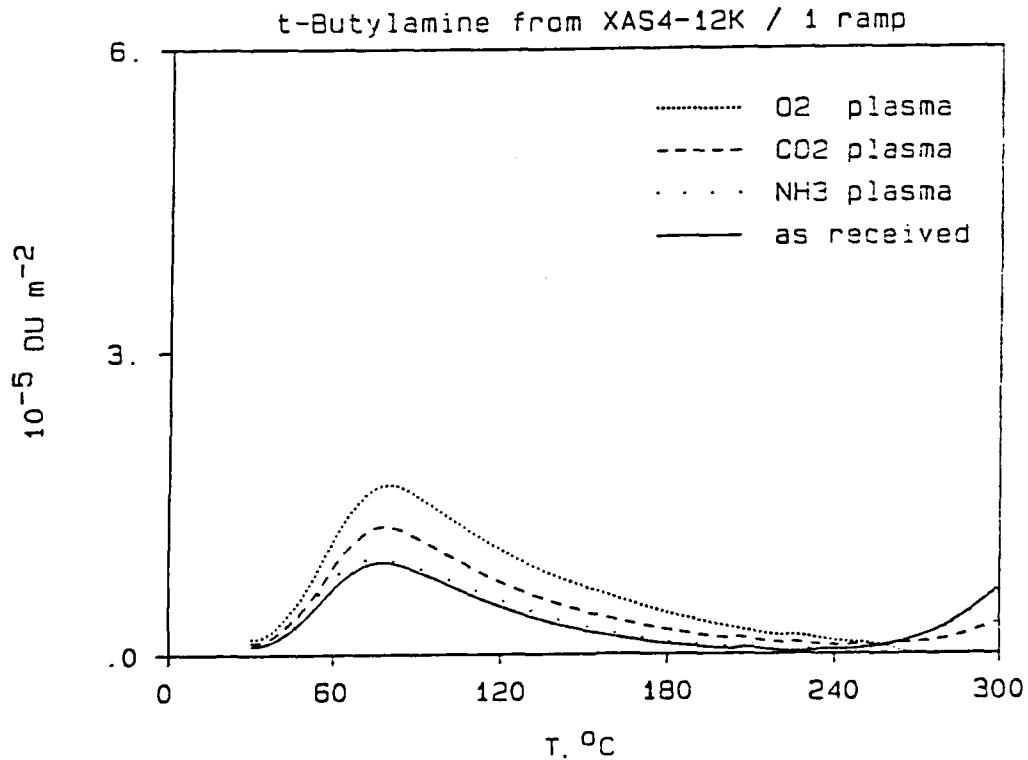


Figure 29. t-Butylamine from XAS4-12K 1 ramp.

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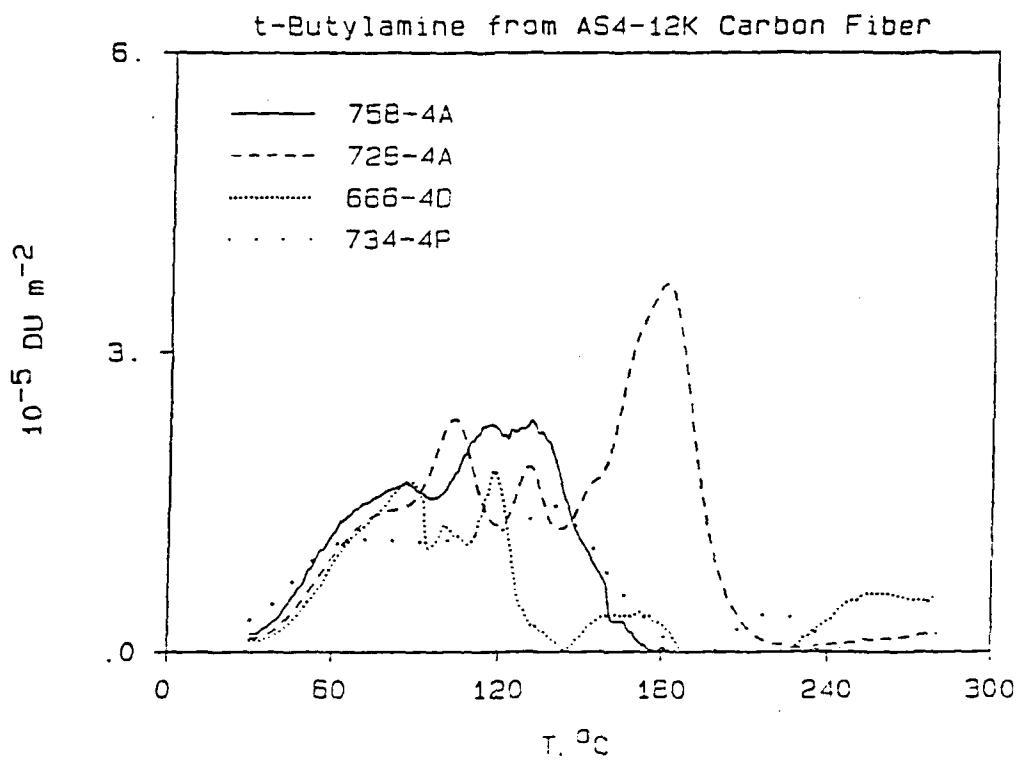


Figure 30. t-Butylamine from AS4-12K carbon fiber.

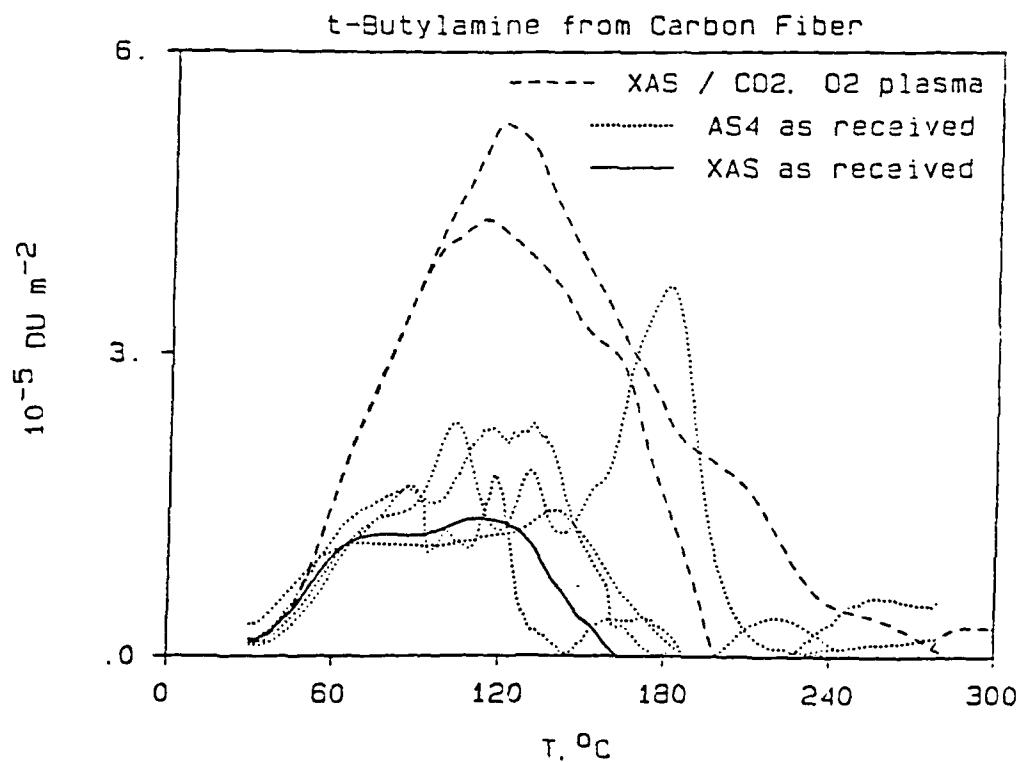


Figure 31. t-Butylamine from carbon fiber.

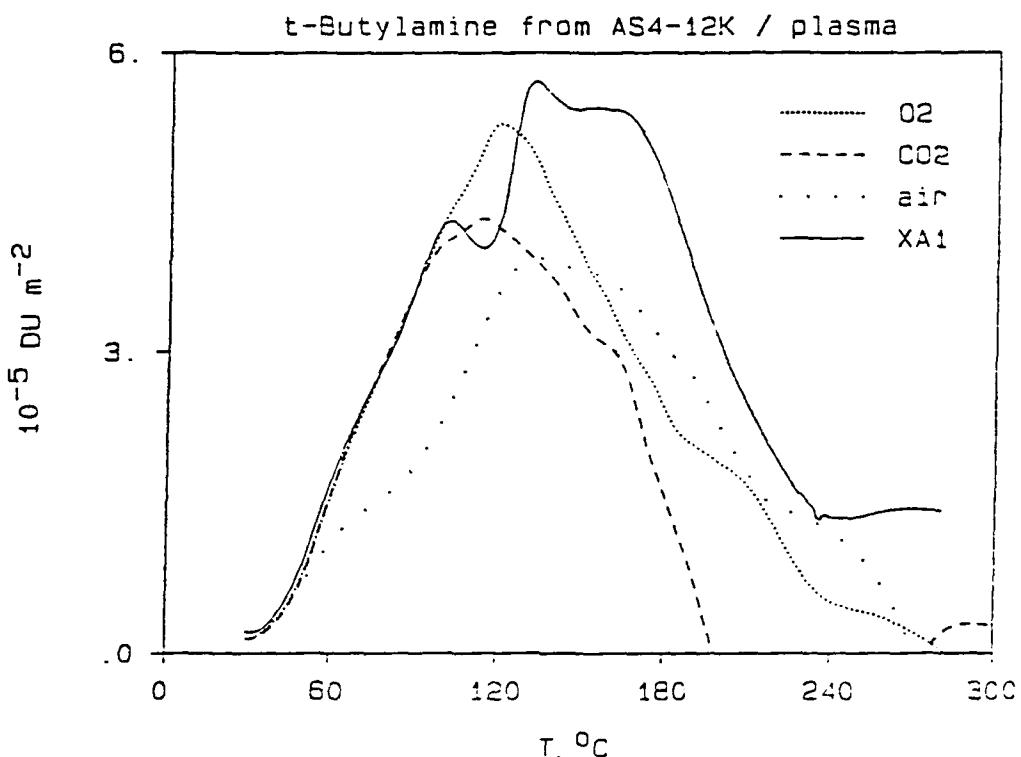


Figure 32. t-Butylamine from AS4-12K plasma treated.

t-butylamine is used as a probe to evince surface acidity; t-butanol is used as an acidic probe to describe surface basicity in a symmetrical fashion. Monolayer isotherms for the acidic probe on control and plasma treated carbon fiber surfaces are displayed in Figure 33. O_2 and CO_2 plasmas augment the surface concentration of weakly basic sites, as expected from previous work [1, 2]. NH_3 plasma effects no significant change in surface basicity.

Historical isotherms for t-butanol on AS4 carbon fiber (Figure 34) are experimentally indistinguishable from those on control and NH_3 plasma treated XAS4 specimens (Figure 35). Figures 36 and 37 show representative adsorptive energy distributions for t-butanol on control and O_2 plasma treated AS4 fiber, respectively. Table VIII lists surface area fraction of high energy sites for all AS4 specimens. Figure 38 shows that high energy surface basicity is augmented to some extent by the oxidative plasmas, and not at all by NH_3 plasma treatment.

Historical AS4 polytherms for t-butanol desorption (Figure 39) are not significantly different from those from AS4 control or NH_3 plasma treated fiber (Figure 40). The main inference from both the physisorption (monolayer isotherm) data and the chemisorption data (polytherms) is that NH_3 plasma treatment has no appreciable effect on the surface energetics of carbon fiber.

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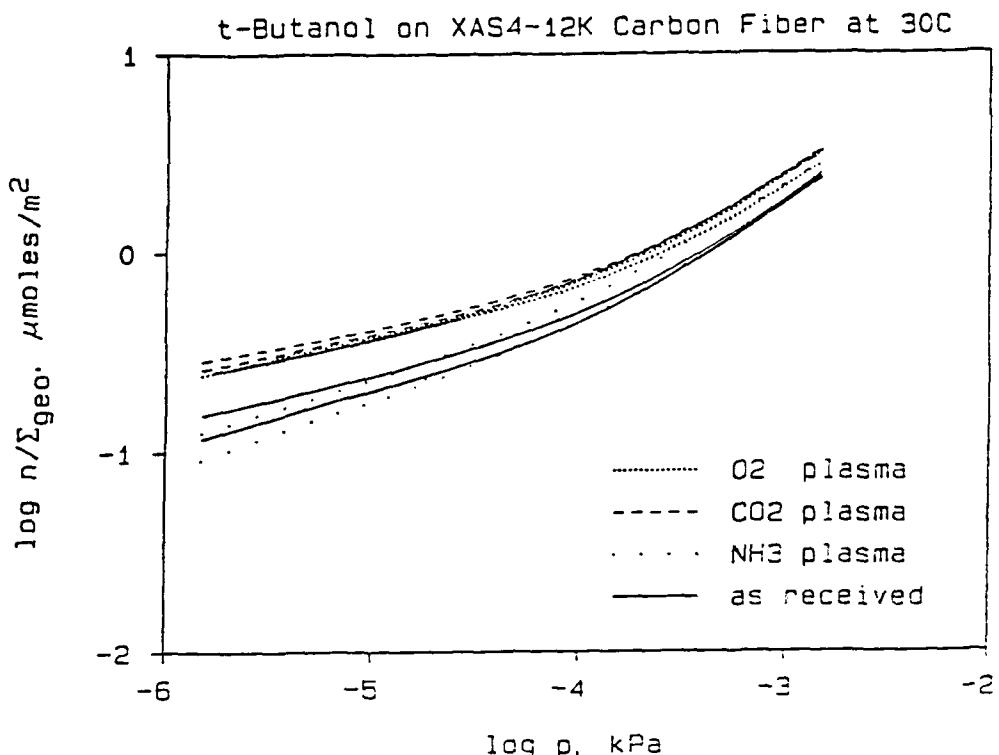


Figure 33. t-Butanol on XAS4-12K carbon fiber at 30°C.

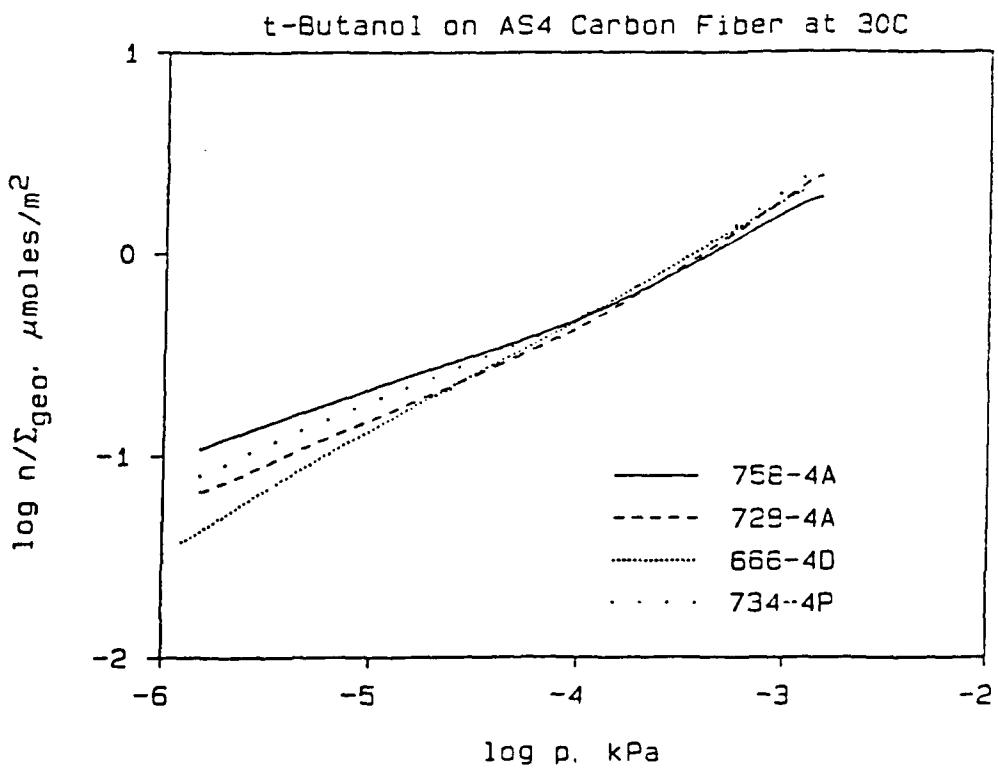


Figure 34. t-Butanol on AS4 carbon fiber at 30°C.

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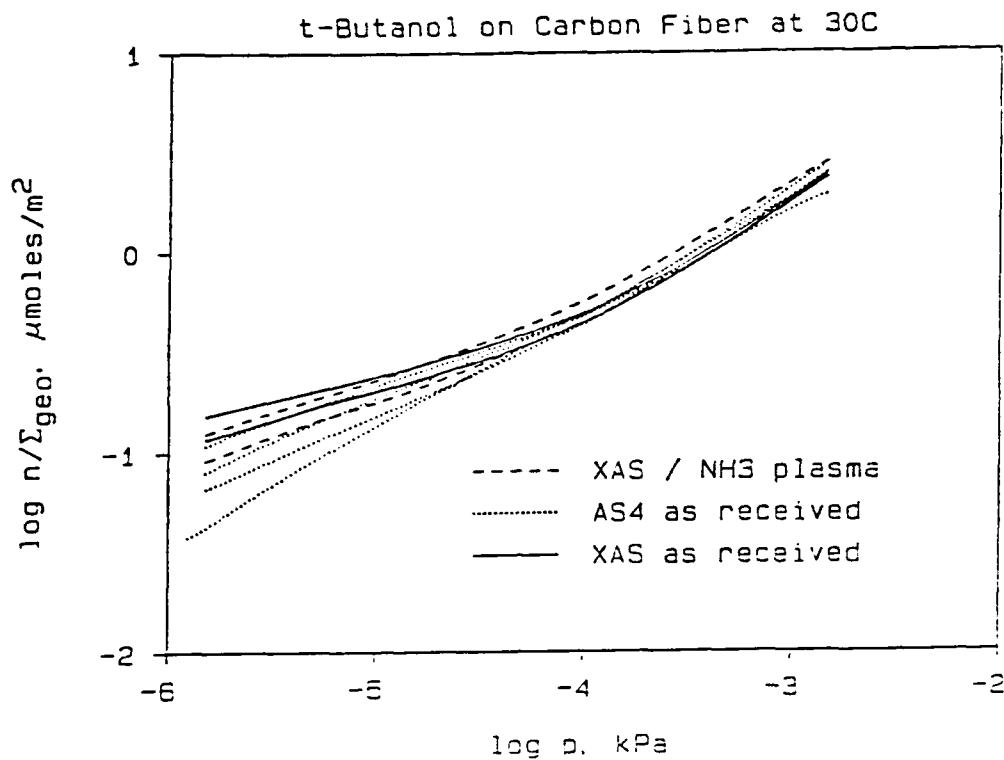


Figure 35. t-Butanol on carbon fiber at 30°C.

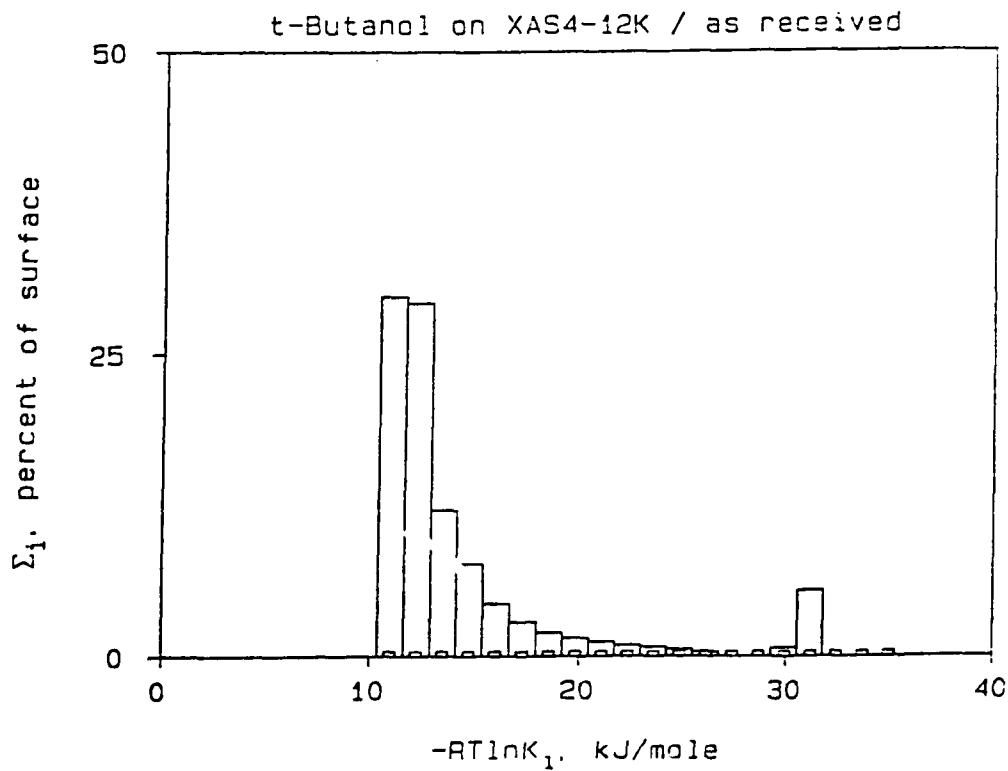


Figure 36. t-Butanol on XAS4-12K as received.

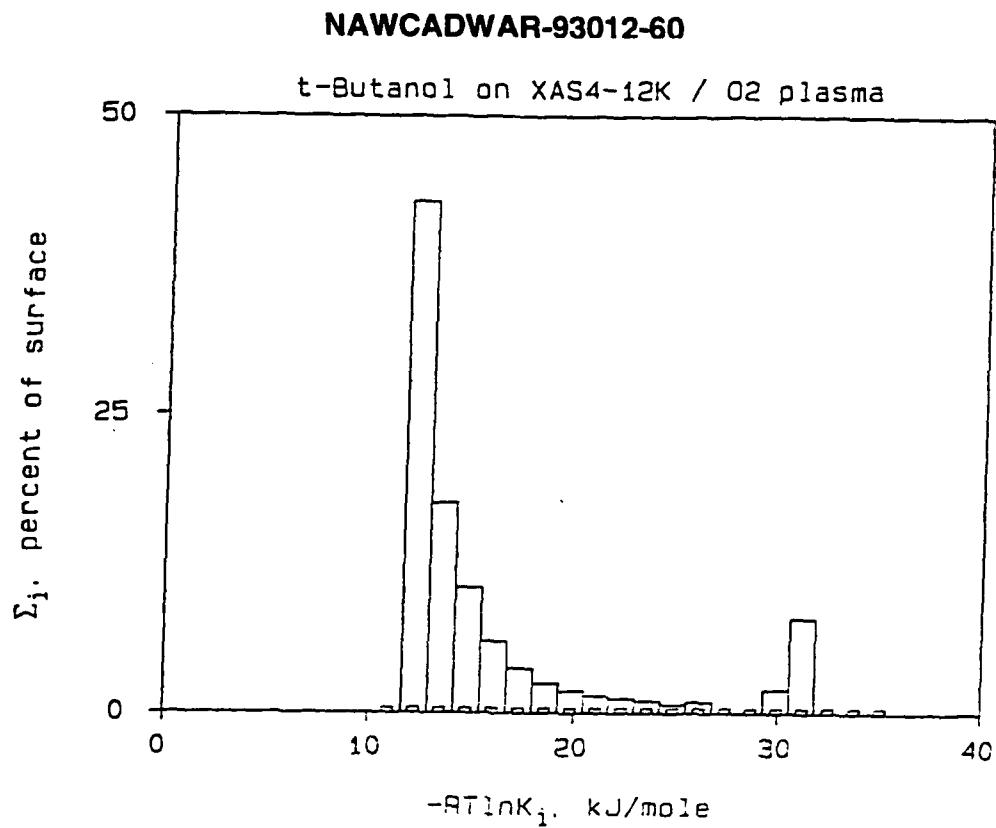


Figure 37. t-Butanol on XAS4-12K oxygen plasma.

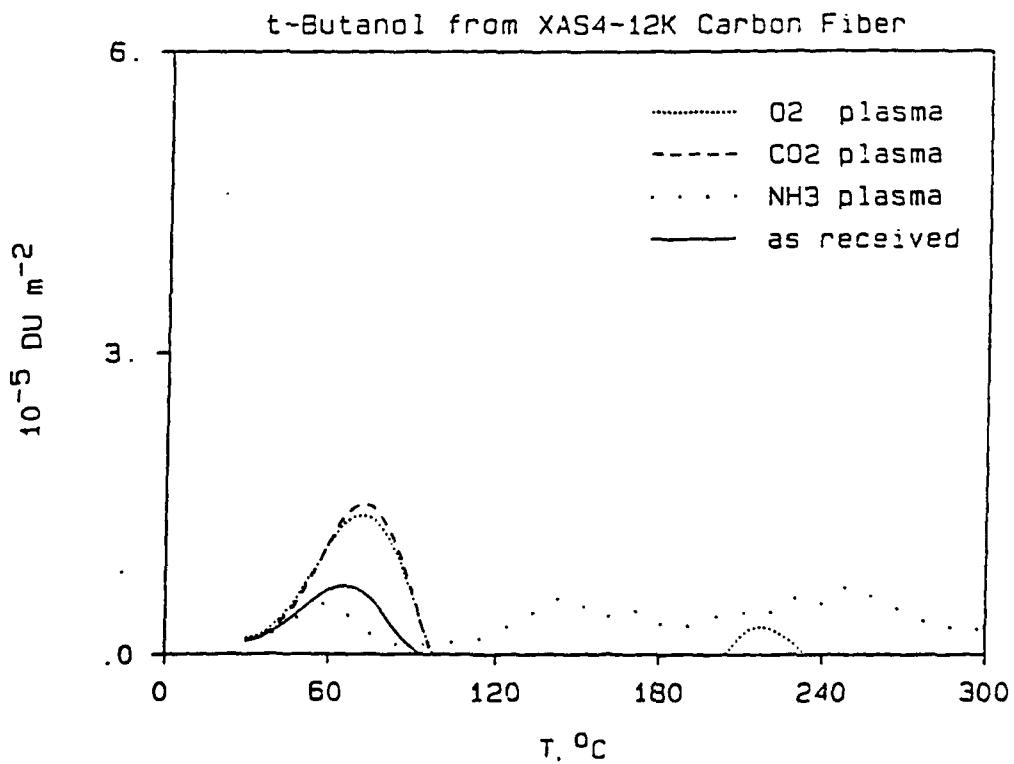


Figure 38. t-Butanol from XAS4-12K carbon fiber.

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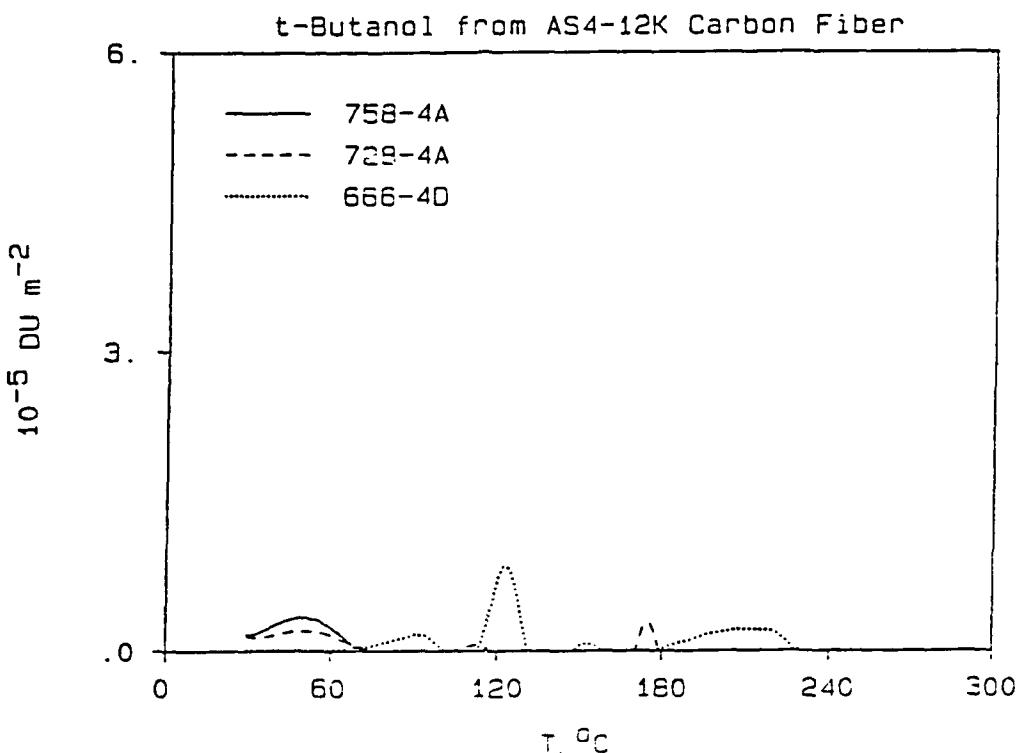


Figure 39. t-Butanol from AS4-12K carbon fiber.

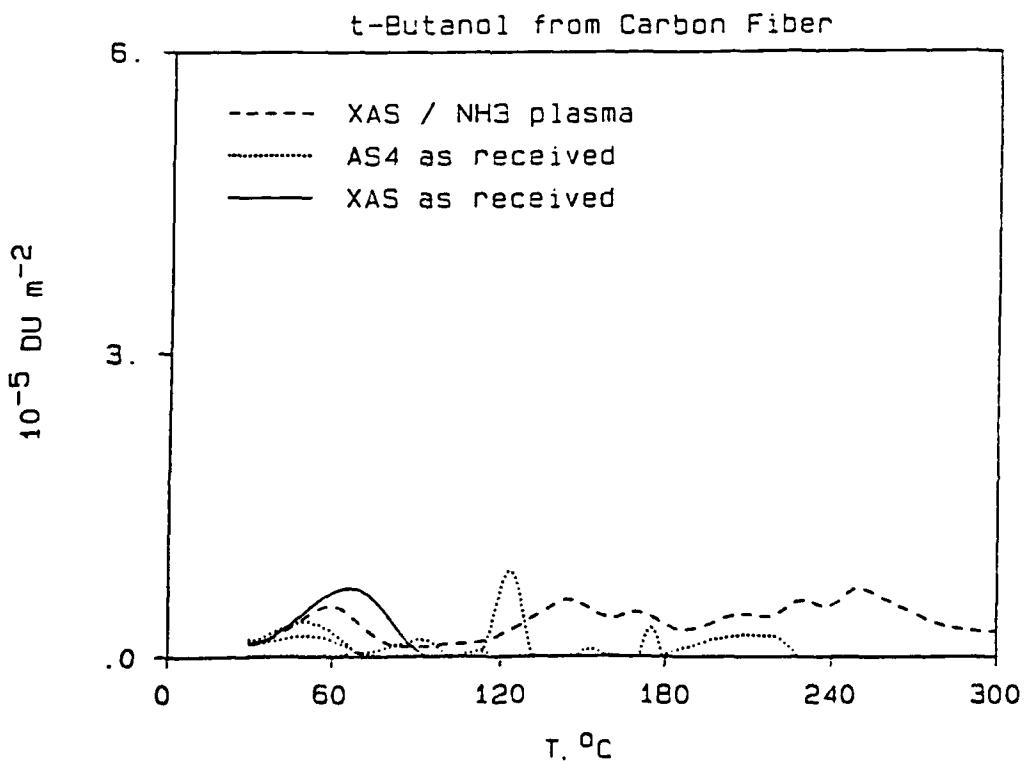


Figure 40. t-Butanol from carbon fiber.

TABLE VIII. t-BUTANOL ON CARBON FIBER

<u>IGC</u>	$\Sigma_{\text{chemisorption}} (\%)$	
AS4 / as received	6.2	
AS4 / NH ₃ plasma	4.2	
AS4 / CO ₂ plasma	7.2	
AS4 / O ₂ plasma	7.9	
<u>PTD</u>	Volume Desorbed (10^{-5} DU °C/m ²)	T _{max} (°C)
XAS4 / as received	27.7	65
1 ramp	34.0	70
AS4 / NH ₃ plasma	18.2	60
	31.1	60
AS4 / CO ₂ plasma	55.7	70
	38.5	70
AS4 / O ₂ plasma	55.5	70
	37.6	70
AS4 / air plasma	216.6	70

Figure 41 displays t-butanol polytherms from previously ramped AS4 fiber. Thermal treatment seems to have less effect on surface basicity than on surface acid functionality (see Tables VII and VIII).

The effect of air plasma treatment is contrasted with that of the other plasmas in Figure 42. The very substantial desorption volume for the acid probe resulting from air plasma suggests that nitrogen plasma should be considered in future work directed at augmenting the surface basicity of carbon fiber.

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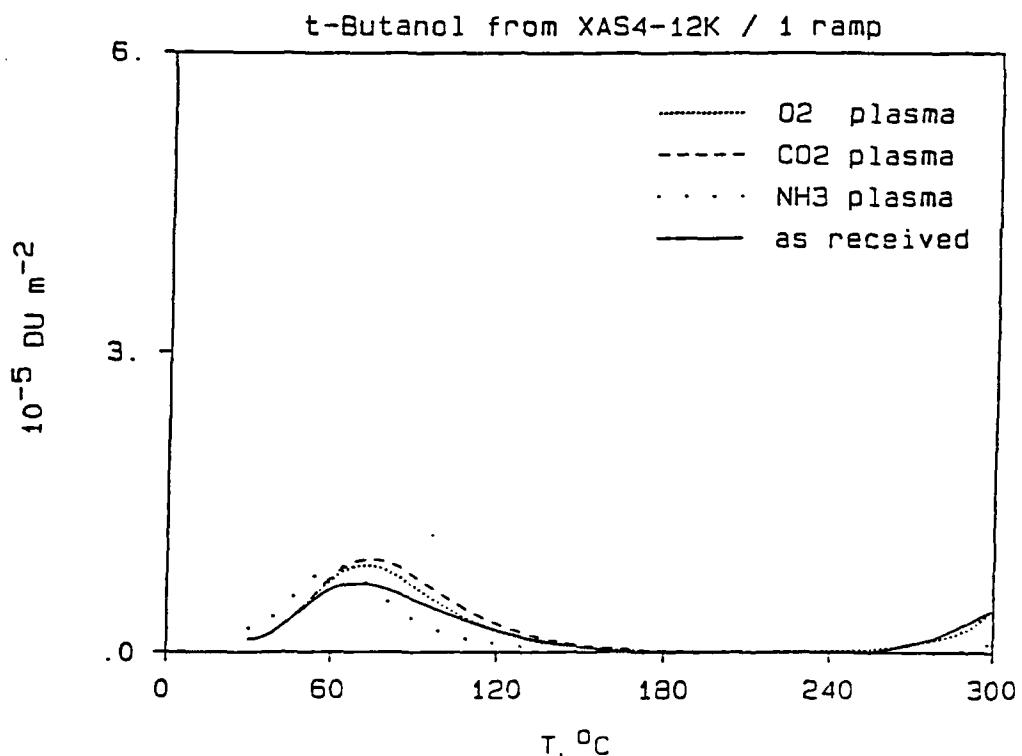


Figure 41. t-Butanol from XAS4-12K 1 ramp.

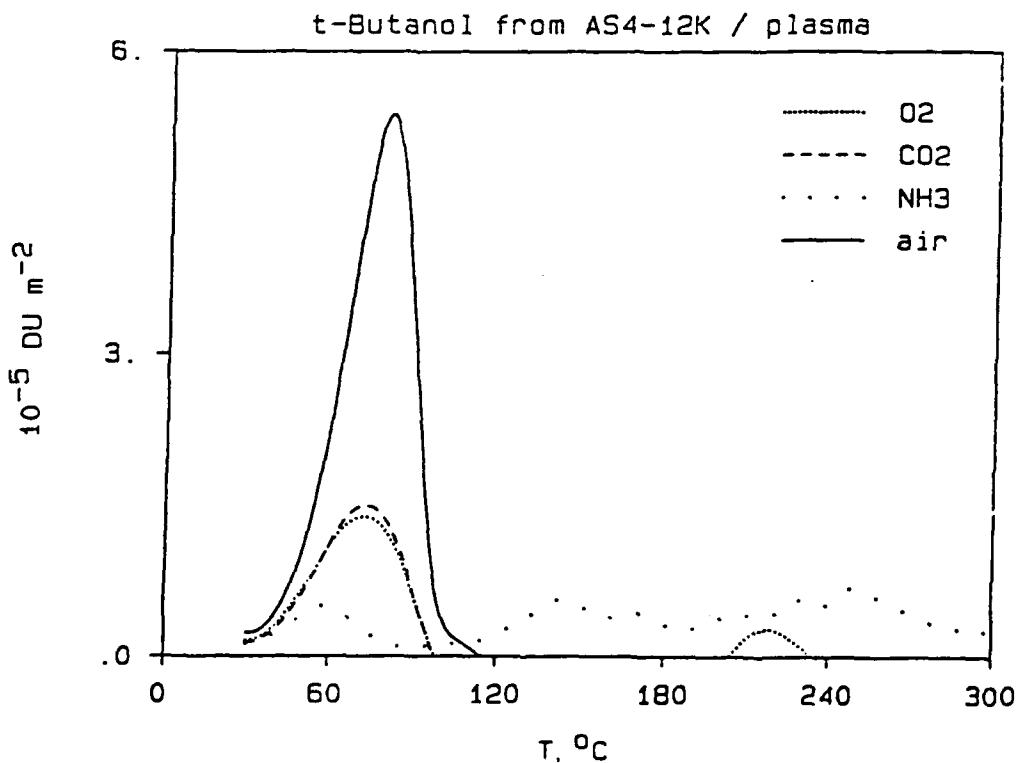


Figure 42. t-Butanol from AS4-12K plasma treated.

Fiber Surface Area Measurements

The surface area of the plasma treated AS4-12K carbon fibers that were delivered to NAWC was measured by nitrogen porosimetry; the experimental lower limit of nitrogen porosimetry is 1 m²/g. The surface area per gram for the AS4-12K fiber untreated and ammonia, oxygen and carbon dioxide plasma treated are given in Table IX. Considering the experimental uncertainties, the surface area of the oxygen and carbon dioxide treated fibers are only slightly greater than the untreated and ammonia treated fibers.

TABLE IX. SURFACE AREAS OF THE UNTREATED AND PLASMA TREATED AS4 FIBERS

Fiber	Surface Area, m ² /g
Untreated	1.8325 ± 0.0797
Ammonia Plasma	1.8211 ± 0.0949
Oxygen Plasma	8.2260 ± 0.8126
Carbon Dioxide Plasma	8.2200 ± 0.5845

Task 4 - Properties of Thin Films

The mechanical properties such as modulus of thin coatings are largely unknown. This task objective was to measure the development of bulk and shear modulus of the thin polymer films using a surface acoustic wave (SAW) device. This effort was conducted jointly with Dr. Tony Rico and Dr. Steve Martin of Sandia National Laboratories.

Two polymer systems were examined. The first, Epon 828 cured with m-phenylene diamine in a ratio of approximately 100:15.5, was varied around the stoichiometric ratio to examine the effect of curing agent concentration on thin film elastic properties. This coating was unsuccessful because the SAW device lost electrical contact during heatup. This is a SAW device system limitation.

The second, a room temperature curing system Epon 828 cured with T403, could not be applied to the SAW crystal in a thin enough coating thickness to obtain the desired viscoelastic properties. Attempts to reduce film thickness by thermal heating of the mixture prior to application and spin coating were not successful. Spin coating the polymer from solution was also not successful. Data of frequency vs. amplitude and time that was reported in one of the progress reports was for a system developed at Sandia and illustrated the data that was expected for this system.

Problems that were encountered during the formation of thin polymer fibers on the SAW transducers prevented this task from being accomplished.

Conclusions

Prior TPL experience is that plasma treatment always renders carbon fiber surfaces amphoteric, implanting both acidic and basic functionality. The effect of changing plasma chemistry and conditions is therefore to shift the balance towards more acidity or more basicity.

1. Non-aqueous titration analysis of the plasma treated AS4-12K carbon fibers that were delivered to NAWC measured surface site concentrations of 0.169 NH₃ sites/nm², 1.065 acid sites/nm², and 1.110 acid sites/nm² for the optimized ammonia, oxygen, and carbon dioxide plasma treatments, respectively.
2. ESCA analysis revealed that the N and O content on ammonia and oxygen/carbon dioxide treated AS4-12K carbon fibers, respectively, that were delivered to NAWC are significantly greater than observed in the untreated fibers. High resolution ESCA spectra indicate that the graphite surface is attacked and converted to esters and/or carboxylic acid moieties (the high energy C_{1s} peak is 50 percent greater) for the oxygen and carbon dioxide plasma treated fibers.
3. Plasma treatment does not increase the surface rugosity on a scale detectable by molecules the size of pentane (Figure 15). Nitrogen sorption indicates that the surface area of the oxygen and carbon dioxide treated fibers are only slightly greater than the untreated and ammonia treated fibers.
4. Sample-to-sample precision for IGC measurements is sufficient to discriminate between t-butylamine isotherms obtained on plasma treated and standard electrooxidized carbon fiber. O₂ and CO₂ plasmas are equally efficacious at implanting surface acidity; ammonia plasma treatment has no effect (Figure 16).
5. Ramping to 300°C does not affect dispersion force interactions and weak to medium strength acid sites (Figures 17, 18).
6. Carbon fiber surfaces as received are contaminated with adventitiously adsorbed organic material. Plasma treatments partially remove this material and ramping totally removes these contaminants (Figure 19).
7. Historical t-butylamine isotherms on AS4 carbon fiber lie between those on AS4 samples as received and after O₂ and CO₂ plasma treatment (Figure 21).
8. O₂ and CO₂ plasmas remove surface contaminants partially, and implant additional acidic and basic functionality. These

combined effects extend the range of PTD analysis above 250°C, as compared to the 200°C upper limit for carbon fiber as received (Figures 24 to 27).

9. O₂ and CO₂ plasmas greatly augment the chemisorptive envelope for t-butylamine, and to an equivalent degree. NH₃ plasma has no such effect (Figure 28).
10. Temperature ramping to 300°C diminishes the chemisorptive envelope for t-butylamine almost completely above 120°C, and to a minor extent below 120°C (Figure 29).
11. Historical t-butylamine polytherms are equivalent to that from untreated AS4 fiber. Fiber treated with O₂ and CO₂ plasmas show much greater chemisorptive capacity for the basic probe (Figures 30, 31).
12. t-Butylamine polytherms resulting from O₂, CO₂, and XAl plasma treatment are equivalent. Air plasma treatment shows less chemisorptive capacity in the low temperature range (Figure 32).
13. t-Butanol isotherms show that dispersion force interactions and weak to medium energy basic sites are not changed by NH₃ plasma treatment, and are augmented by O₂ and CO₂ plasmas (Figure 33).
14. Historical t-butanol isotherms on AS4, untreated XAS, and NH₃ plasma treated AS4 carbon fiber are all equivalent (Figures 34, 35).
15. NH₃ plasma treatment does not change the chemisorptive capacity of the surface for t-butanol, as do treatment with O₂ and CO₂ plasmas (Figure 38).
16. Differences in the chemisorptive capacity of AS4 carbon fiber as received, and NH₃ plasma treated are similar, and equivalent to that of historical AS4 carbon fiber (Figure 41).
17. Ramping does not affect basic sites significantly (Figure 41).

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1. S. P. Wesson and R. E. Allred, in: Inverse Gas Chromatography, D. R. Lloyd, T. C. Ward, and H. P. Schreiber (Eds.), ACS Symposium Series 391, p. 204, ACS, Washington, DC (1989).
2. S. P. Wesson and R. E. Allred, J. Adhesion Sci. Technol. 4, 277 (1990).

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